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A PROPOSAL TO NSF FOR A CdS-Cu_2S PHOTOVOLTAIC CELL DEVELOPMENT PROGRAM

R. S. Berg
D. M. Mattox

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RESEARCH APPLIED TO NATIONAL NEEDS (RANN)

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Name of Organization (including Branch title, if any)

Albuquerque, New Mexico 87115
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A PROPOSAL TO NSF FOR A CdS-Cu_2S PHOTOVOLTAIC CELL DEVELOPMENT PROGRAM
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A PROPOSAL TO NSF FOR A CdS-Cu_2S PHOTOVOLTAIC CELL DEVELOPMENT PROGRAM

R. S. Berg and D. M. Mattox
Sandia Laboratories, Albuquerque, New Mexico 87115

ABSTRACT

Photovoltaic devices for direct solar to electrical energy conversion can potentially furnish large amounts of electrical energy if problems associated with fabrication and lifetime can be solved. In this proposal to the National Science Foundation, Sandia Laboratories is requesting funding for a three year program to 1) study the material and process problems associated with the production of high quality CdS-Cu_2S solar photovoltaic cells using Chemical Ion Plating and 2) develop techniques for the large scale production of such cells. The program is designed to combine an extensive developmental background in Ion Plating, expertise in materials and device characterization, and a broad base of analytical facilities. The first year of the program will address the application of Chemical Ion Plating techniques to CdS and Cu_2S and a characterization of films produced by the technique The first year's results will then be utilized in the second year of the program to study doping and property modification techniques. Depending on the above results, the third year of the program will be devoted to the fabrication and testing of devices.

Throughout the proposed program, extensive use will be made of the wide range of analytical capabilities at Sandia Laboratories. It is further proposed that these facilities could be made available to other laboratories on a cooperative basis for the purpose of extending and standardizing the testing performed by the several researchers in this field.

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A. PROPOSAL SUMMARY

Photovoltaic devices for direct solar to electrical energy conversion are of great interest due to the availability of solar energy and the simplicity of direct conversion techniques. These devices can potentially furnish large amounts of electrical energy with minimal environmental damage and at low overall cost. Although the thin film CdS-Cu_2S cell is one of the more promising photovoltaic devices, it suffers from several problems associated with cell fabrication and lifetime. The object of this research program is to address the material and process problems for fabricating high efficiency low degradation CdS-Cu_2S solar cells with high yields using the technique of Chemical Ion Plating. Chemical Ion Plating is a technique which is derived from the more general process of Ion Plating, which is an atomistic deposition process in which the substrate is subjected to a high energy ion flux sufficient to cause appreciable sputtering before and during film deposition. When the discharge that supplies the ions also contains volatile compounds of constituents desired in the film, the process is called Chemical Ion Plating.

In the proposed program, Chemical Ion Plating techniques for the deposition of both CdS and Cu_2S will be developed. These techniques have been applied to numerous materials for the purpose of controlling morphology, stoichiometry, and other important properties. Initial experiments indicate that similar results can be expected with CdS and Cu_2S. These techniques could also be applied to other semiconductors.

Using the results of the deposition experiments, Chemical Ion Plating techniques will then be applied to doping of CdS and Cu_2S films during deposition. Both CdS and Cu_2S have been doped with a variety of dopants for the purpose of controlling and modifying film properties. Chemical Ion Plating techniques have

been used to dope other materials, and are, in principle, applicable to a much larger variety of dopants than other techniques.

Finally, these techniques will be used to fabricate complete devices. Both front and back-illuminated devices will be fabricated using a variety of presently available materials as substrates and contacts. The cells will be tested under a variety of field and laboratory conditions. Throughout the program the technologies developed will be examined for their applicability to large scale production of solar cell devices.

At each step in the proposed program, extensive use will be made of the various analytical facilities available at Sandia Laboratories. These facilities are among the most extensive in the world. As a means of extending research and standardizing analytical techniques, it is proposed that these facilities also could be made available to other laboratories on a cooperative basis. Because of these existing facilities, this proposal contains no start-up or equipment capitalization costs.

It is estimated that a three year (minimum) program will be required for the completion of the proposed program. First year funding is set up at $305,000 for a five man-year effort. The proposal contains a detailed accounting of the tasks to be accomplished, the personnel involved, and the estimated time schedule. In addition, decision points and choices available are enumerated. The relation of this work to related activity at Sandia Laboratories and at other laboratories is discussed briefly.

B. RESEARCH OBJECTIVES

Introduction

There are numerous discussions of the utilization of photovoltaic devices in the literature. Some analysts estimate that significant amounts of the total electrical energy needs of the country will one day be generated by photovoltaic devices.[1] This prospect depends primarily on the economics of their production, installation, maintenance, and their lifetime. This outlook is true for both of the principle devices: Si single crystal and thin film CdS-Cu_2S solar cells.

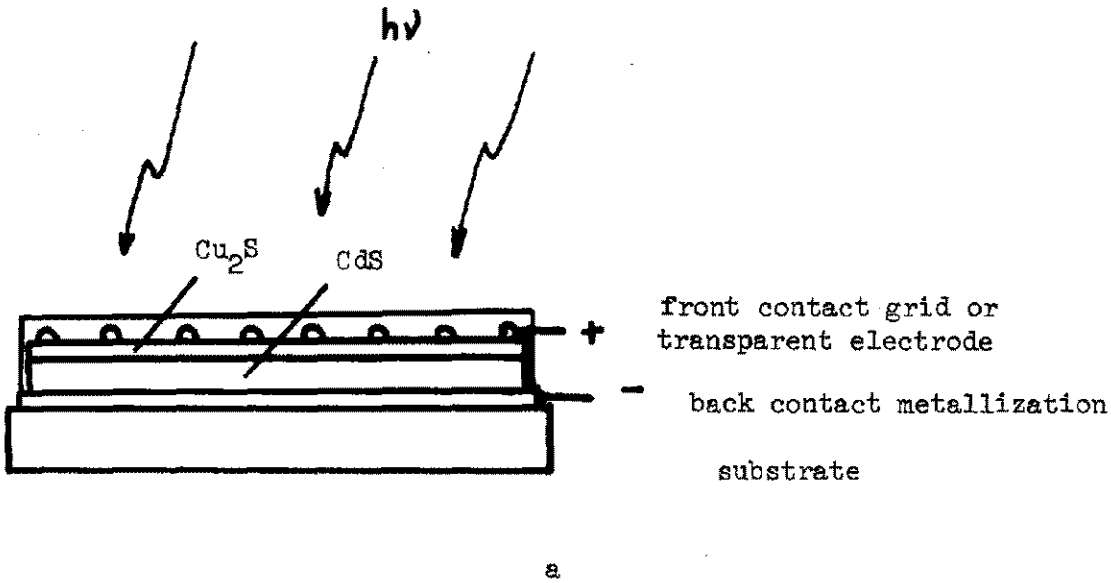
Direct gap semiconductors are theoretically preferable in photovoltaic devices because of the generally sharper optical absorption edge at the energy gap compared to indirect gap semiconductors. The resulting higher absorption allows the use of very thin films of material in the device. Heterojunction solar cells using direct gap semiconductors have an additional advantage over common homojunction cells in that optical adsorption can be controlled so that the absorption of incident radiation occurs within a narrow region adjacent to the junction. Polycrystalline materials can therefore be used in the cell fabrication since photo-carriers can still generate a current in spite of their short lifetime and low mobility. The use of thin film technology and small amounts of material per unit power output give the possibility of low cost, high volume fabrication of solar cells.[1,2,3]

Of the hetrojunction photovoltaic cells, the most widely considered is the CdS-Cu_2S cell. In this system the CdS is the n-type material with E_g = 2.4 eV and the Cu_2S is the p-type material with E_g = 1.2 eV. Several possible band diagrams for this cell have been suggested.[4,5] This thin film cell has been under intensive development in England,[6] France,[7] and other European laboratories and is used in some of the French satellite systems. Work has also been done on this

system in several U.S. laboratories.[8,9] Generally, it is reported that cells of 4-6% efficiency can be prepared without great difficulty, though production yield can be a problem and there are several existing degradation mechanisms, particularly in poorly fabricated and/or protected cells.[10]

Conventional front illuminated devices for terrestrial applications use a zinc-coated copper[9] or metallized flexible polymer[11] such as FEP teflon, Mylar, or Kapton, for the substrate and back contact. The CdS layer may then be deposited by a variety of techniques such as vacuum deposition[12] or chemical spraying.[13] A thickness of about 10 to 30μm is normally required for reasons related to cell degradation and yield, although thicknesses up to 50μm for evaporated devices[14] and down to about 2μm for sprayed devices[13] have been reported. A film resistivity in the neighborhood of 10 Ω-cm is desired. The Cu_2S is then formed either by chemical spraying,[13] an evaporation-annealing process,[15] or ion exchange[16] to a thickness of a few tenths of a micrometer. A front electrode of gridded copper is deposited or glued onto the surface.[12] Figure 1a shows the design of a typical front illuminated CdS-Cu_2S cell.

There have also been several recent suggestions into the possibility of fabricating new types of back-illuminated cells. Originally, these cells were felt to have inherent limitations due to the necessity of dry forming the diode.[1] However, the use of an optically transparent electrically conductive coating such as SnO_x, $In_xSn_{2-x}O_y$, or Cd_2SnO_4 for the back contact deposited on glass or plastic, and a somewhat thinner CdS layer have given back illuminated cells more promise. The Cu_2S layer can then be protected more effectively by a continuous metal film, while high optical absorption is maintained near the junction.[16] Figure 1b shows the design of a back illuminated cell.



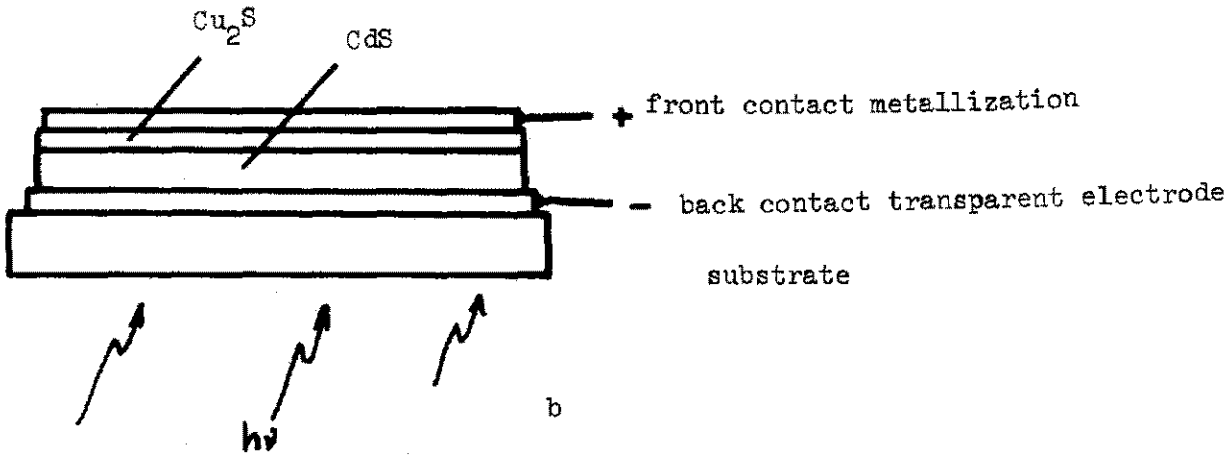


Fig. 1 Basic construction for a) front illuminated cell and b) back illuminated cell.

Statement of the Problem

Many of the estimates of CdS-Cu_2S cell utilization are based on continued break-throughs in both fabrication techniques and cell lifetime.

The research and development program proposed here is directed at controlling and reducing the effects of the degradation mechanisms and fabrication problems that have hindered the utilization of CdS-Cu_2S solar cells. The principle degradation mechanisms operational in CdS-Cu_2S cells have been identified. They are:

1. Oxidation-reduction reactions in the Cu_2S layer. These reactions result in a change to sub-stoichiometric Cu_2S, and are the result of thermal- and photo-assisted oxidation[14,17] or electrochemical reduction.[18] They are believed to cause a reduced optical absorption near the junction and reduced short circuit current.
2. Field enhanced diffusion of copper through the junction.[15,19] This is believed to result in an increase in the CdS resistivity near the junction. It also can produce copper structures in the junction and CdS layer, which cause decreased shunt resistance and eventually shorting of the cell.
3. Thermally and optically stimulated reversible changes in the junction region affecting the Cu_2S stoichiometry[11] and the CdS.[20] These may be reversed by special processing.
4. Film inhomogeneities which give rise to hot spots[9,21] and enhance Cu_2S decomposition and Cu diffusion.

Several of these degradation mechanisms are enhanced by non-stoichiometric Cu_2S and a low density CdS layer. A general problem of poor cell reproducibility and poor production yield[11,18] exists because of the lack of deposition control.

Possible remedies to these problems which have been suggested involve:

1. Operating the cell in a vacuum,[14] an inert atmosphere,[22] or hydrogen environment[2] to reduce oxidation.
2. Limiting the cell voltage to below the maximum power voltage and limiting the operating temperature to eliminate electrochemical decomposition and Cu diffusion.[19]
3. Incorporating chemically active dopants, or "scavangers" into the CdS layer to reduce or eliminate the effect of diffusion of copper atoms.[7]
4. Improving processes and process controls[2] to obtain high density CdS layers, stoichiometric Cu_2S, and greater film uniformity over large areas.

Specific Program Objectives

The object of this research program is to address the problems associated with the semiconductor materials and the processes for fabricating high quality low degradation CdS-Cu_2S thin film solar cells with a goal of obtaining as high a yield and as low a cost as possible using Chemical Ion Plating. The capabilities and flexibility of this technique could provide a significant part of the advancement needed for the practical utilization of CdS-Cu_2S photovoltaic cells. In particular, the following aspects will be studied:

1. Control of CdS stoichiometry and film morphology using Chemical Ion Plating techniques.
2. Control of the electrical properties of CdS by doping during Chemical Ion Plating.
3. Study of copper diffusion rates in Chemical Ion Plated CdS as a function of film morphology and density.

4. Study of the effect of chemically active dopants or "scavangers" introduced by Chemical Ion Plating, on the diffusion of copper through CdS films.
5. Control of stoichiometry and structure of Cu_xS films using Chemical Ion Plating techniques.
6. Examine effects of non-stoichiometry and doping on phase composition and stability of Cu_xS.

The objectives of the first 12 months of this program will be to develop the Chemical Ion Plating technology applicable to cadmium sulfide and copper sulfide, determine the effect of the CIP deposition process on the electrical and morphological properties of CdS, and determine the effect of the CIP processing on the stoichiometry, phases and phase stability of Cu_xS. Longer term objectives will involve the fabrication of solar cells and optimizing film properties for this purpose.

C. RESEARCH PLAN

This proposal encompasses work involving two important areas. First is the versatility and adaptability of Chemical Ion Plating as a materials deposition technique. This technique and its application have received extensive development at Sandia Laboratories. Second is the experience and analytical capabilities available at Sandia Laboratories which will be utilized in the study of materials properties and degradation mechanisms.

Chemical Ion Plating (CIP) is a technique derived from conventional Ion Plating,[23] in which a developing film is subjected to ion bombardment sufficient to cause appreciable sputtering of deposited material before and during deposition. When any gas phase constituent or new component desired in the film is added to the discharge, the technique is called Chemical Ion Plating. The sputtering is controlled by the discharge parameters (principally gas composition and pressure, and discharge voltage) and the substrate bias. The source may be any method for injecting material into the discharge region, but is usually either a conventional physical vapor source or a sputtering cathode.

The effects of ion bombardment during deposition (Ion Plating) on the structure, morphology, and electrical properties of films have been studied extensively in this laboratory. It has been found in experiments at Sandia Laboratories that ion bombardment during deposition can increase the density of the deposited material, disrupt the columnar morphology usually associated with thick deposited films, and modify the crystal structure and orientation of the deposited film.[24] Ion bombardment can also drastically modify both the stresses imposed during deposition[25] and the stoichiometry[26] of certain kinds of films. Chemical Ion Plating techniques have recently been applied to the deposition of CdS, with comparable results.[27] (Refer to attachments 1-4.)

Areas of Required Research

Task 1. Properties of CIP CdS

The development of CIP, a deposition system, involves the design of components for the various system functions, such as substrate table and holder, discharge electrodes, shielding, etc. There have been several studies performed at Sandia Laboratories setting forth the requirements for such a system.[28,29,30] Although deposition system design studies often have been overlooked in deposition experiments, it has been shown that proper design is a very important aspect of achieving quality, reproducible results. In general, a very clean system with high throughput is required to prevent excessive contamination of the depositing film. In addition, the geometry and spacing of the source, substrate, and other electrodes must be carefully chosen since they determine the discharge properties, film uniformity, and other important parameters. Many of these factors have been implemented in the existing system, and others are being added as required. The capabilities of such systems are also enhanced by the ability to control substrate temperatures and to use either dc or rf discharges and biases. The use of rf is particularly valuable when insulating or poorly conducting films or substrates are required.

The first of two studies to be completed in the initial 12 month contract period is a study of the properties of CIP CdS. There have been numerous studies of the physical properties of CdS.[31-36] CdS is an n-type semiconductor; the source of the carriers being related to a sub-stoichiometric S:Cd ratio. This sulfur deficiency is believed to result in numerous traps and defect complexes in the material.[37]

CdS has been deposited by evaporation, sputtering, and chemical spraying. Evaporation is generally used for depositing photovoltaic devices due to its

generally higher deposition rates and the low resistivities achieved. The low resistivity is one result of the sub-stoichiometric composition, and is often difficult to control. In general, the CdS is deposited at rates sufficient to give the desired resistivity.[38,39,40] Several schemes have been designed to control the composition by using modified sources and dual source systems.[15,38,40,41] However, some of the complexes that control the resistivity are also believed responsible for electrical and optical degradation effects.[20,34,37,42] Chemical Ion Plating has been used to control stoichiometry in several systems,[26,27] including CdS.

Experiments with sputtering of CdS have reduced sulfur deficiencies by adding H_2S to the discharge gas.[43] Sputtering is preferred for photoconductive, acoustoelectric, and several other devices due to the degree of perfection and control of stoichiometry it permits. However, the sputtering of CdS is a relatively slow process. Chemical Ion Plating can be done at much higher rates since the source is not limited to being a sputtering cathode.

Some studies have been performed on chemically sprayed CdS.[35,44,45] Sprayed films have also been fabricated into photovoltaic devices,[13] however, the physical properties of these types of films are not well known.

One of the objectives of this proposal is to obtain relatively high resistivity (stoichiometric), high density CdS at high rates using Chemical Ion Plating. To obtain stoichiometric CdS by vacuum evaporation techniques requires the use of very low deposition rates.[34] The CIP process should result in more reproducible films with greater stability and density. Once these objectives have been established, the films would be doped to the desired levels during deposition. Initial results have been obtained using the CIP technique where CdS is evaporated through a gas discharge containing H_2S, onto a voltage biased substrate which is being subjected to ion bombardment. The bombardment is

controlled by the substrate bias and discharge parameters. It was found that high quality CdS film can be deposited at much higher rates than is possible using standard vacuum deposition techniques.[27] Measurements have indicated a tendency towards higher resistivity in films deposited with large negative biases. The CIP technique avoids many of the stoichiometry problems encountered when trying to vacuum deposit CdS at high rates. It also should allow more reproducible and controllable processing. The effects of ion bombardment have been studied by reflection electron diffraction and were found to include modifications of the c-axis fiber axis dispersion through the film. Much more extensive crystallographic and morphological examinations (using reflection high energy electron diffraction, x-ray analysis, scanning electron microscopy, and other techniques) and electrical analysis (using resistivity, Hall coefficient, Seebeck coefficient, and other measurements) are needed to properly characterize the deposits.

Task 2. Properties of CIP Cu_2S

Another objective of this task is to develop techniques similar to those described in the previous section for a deposition system for CIP Cu_xS. This system will then be used to study and control the phase composition and properties of CIP Cu_xS. The copper-sulfur system has been studied very extensively. Although there are disagreements regarding the details of the phase diagram,[46,47] most researchers report that in the neighborhood of Cu_2S there are several phases present within relatively narrow composition and temperature ranges. The phase diagram is summarized in Fig. 2. Most of the reported studies have been on samples that have been evaporated, diffused, or cooled from high-temperature-mixture melts. However, some studies have been on Cu_xS formed by ion exchange with CdS in a CuCl solution, or dry chemically formed from Cu or CuCl layers vacuum deposited onto CdS and subsequently annealed. These latter processes often form ternary Cu-S-Cd systems,

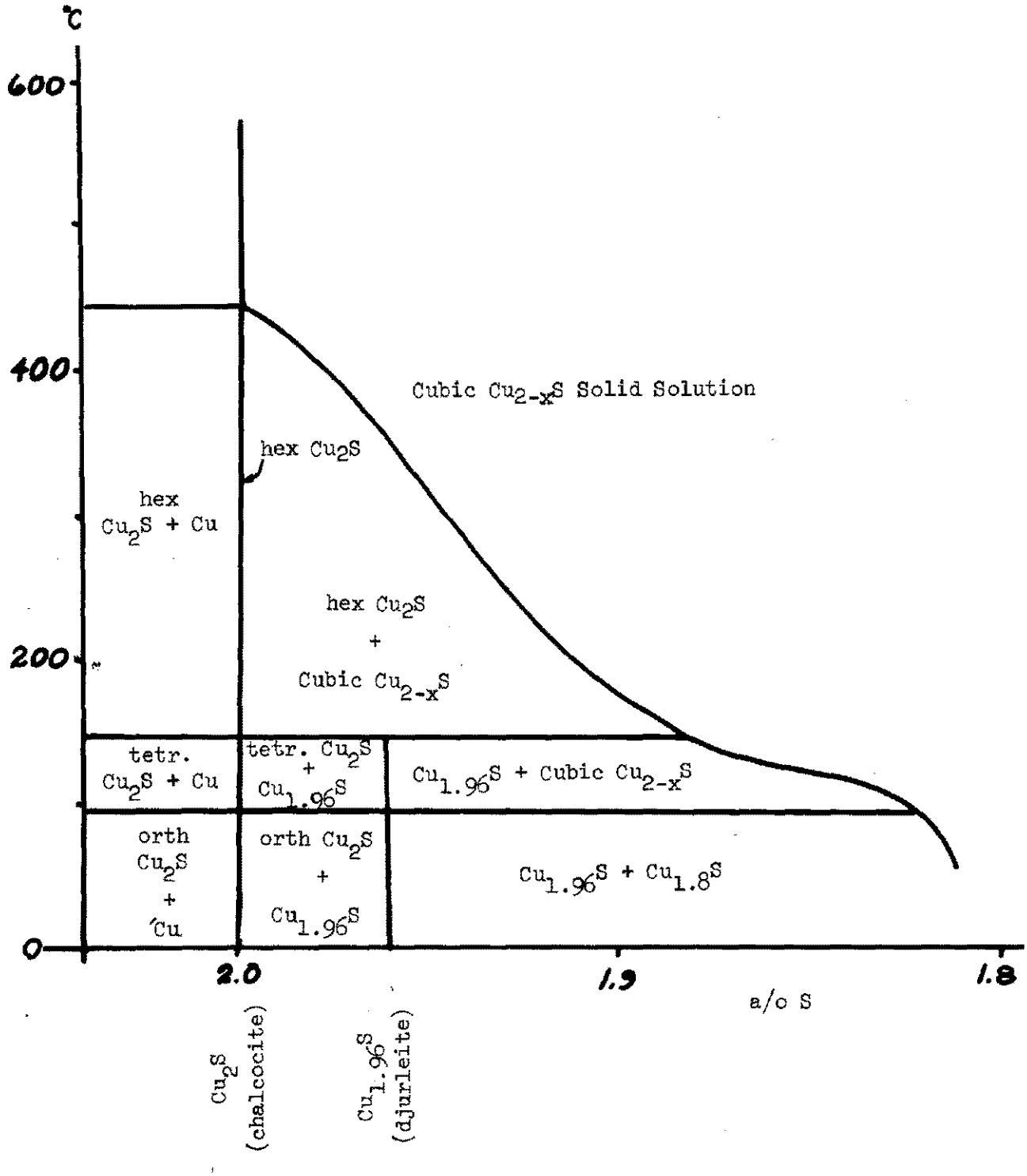


Fig. 2 Copper-Sulphur Phase Diagram
from References 12 and 46

which may account for some of the disagreements on the phase diagram. The morphology of Cu_xS layers has not been studied extensively, and only a few studies are extant.

Although the physical, electrical, and optical properties of the Cu-S system have been studied,[46-51] relatively little is known about their control in thin films of Cu_xS and the relationship between the above properties and film morphology. It is generally believed that Cu_2S (or chalcocite) gives the optimum cell performance by maximizing the short circuit current.[7] There are numerous studies on the effects of various ion exchange fabrication parameters on cell performance.[12,42] In many cells, three or more phases are present within the Cu_xS layer.[52] However, since the cell itself is not well characterized, and the effects of composition profiles and junction morphologies are not known, much of the work has only empirical significance.

The objectives of this task are to control the morphology of Cu_2S through the use of the CIP technique and control of the stoichiometry by adding copper to the discharge gas of the system in a manner similar to that of chemical vapor deposition (CVD). Several volatilizable copper bearing compounds are known[53] and could be used. The same techniques outlined in the previous section will be used to characterize the Cu_2S films.

Task 3. Doping of CIP CdS

There have been many studies on doping of CdS for the purpose of both controlling carrier density and type. Experiments to control the carrier type have been inconclusive.[54,55,56,57] A variety of dopants have been incorporated in CdS by co-evaporation,[58,61] ion-implantation,[55,57] diffusion,[37,38,42,60,61,63-66] and gas phase introduction into a sputtering discharge.[56] The dopants have been used primarily to modify the conductivity, although they have also been used for

defect and recrystallization studies. Table 1 gives a summary of CdS doping information. Since the densified, low defect CdS as produced in Task 1 is intended to have high resistivity, the first phase of this task concerns the introduction of electrically active dopants for the control resistivity by the use of CIP techniques. It is expected that the electrical properties of the resulting films will be more controllable.

The second phase of this task is the introduction of chemically active dopants to control the effects of electrochemical migration of copper into the CdS. It is indicated in the literature that certain dopants will interact with copper in CdS to partially inhibit the effects of diffusion of copper normally associated with degradation.[7] Other impurities concentrated near the interface are believed to act like a diffusion barrier. CIP techniques offer a unique capability to control these effects. The effect of additions of certain dopants on the morphology and structure of the CIP CdS also will have to be studied.

Task 4. Doping of CIP Cu_2S

There are very few experiments on the doping of Cu_2S. Most of them involve residual Cd, Cl, or other impurities incorporated in the Cu_2S during the formation (either ion exchange or dry chemical) of diodes. Another group of dopants in Cu_2S is gas (such as H_2, O_2, H_2O or other environmental gases) diffusing in from the surface of diodes. These have all been empirical studies relating impurity levels to diode terminal properties. The purpose of this task is to study the effects of intentional doping of CIP Cu_2S layers. It is known that in certain metallurgical systems "dopants" have been added for the purpose of stabilizing phases. This has been used in the stabilization of certain phases of the Cu-S system.[46] It may also be possible to dope the Cu_2S to relieve lattice mismatch strains. The versatility of CIP offers an opportunity to study many dopants not otherwise available. If such a dopant could be found for chalcocite (Cu_2S), the diffusion

TABLE I

Impurity	Type	Method	Ref.
Li	Acc.	Coevaporation	58
Al	--	Diffusion	59
P	Acc.	Addition to Sputter Gas Implantation	56,58 55
Cl	Don.	Diffusion	38,42,60,63
Cu	Acc.	Diffusion Grown with Crys.	38,42,59,60,61,63 54,62
Zn	--	Diffusion	59
Ga	Don.	Diffusion Grown with Crys.	60 62
Ag	Acc.	Diffusion Coevaporation	38,59,60 61
In	Don.	Grown with Crys. Diffusion	59,62 60
Pd	--	Diffusion	59
Bi	Acc.	Implantation	57,59
Tm	--	Diffusion	64
Yb	--	Diffusion	65

of Cu might be controlled in such a way as to inhibit the diffusion of copper beyond the normal chalcocite phase transition point.

Task 5. Fabrication of $CdS-Cu_2S$ Solar Cells

Numerous papers have discussed designs for $CdS-Cu_2S$ photovoltaic cells.[7,12,15,17,66,67] Front illuminated cells (Fig. 1a) have received the most attention. Recently, however, considerable interest has developed in back illuminated cells due to the potentially higher efficiency and simplified encapsulation of this design. While the devices are all similar, the details of their construction depend on the fabrication techniques used and the properties desired in the device. For example, some researchers have suggested evaporating 45μm of CdS rather than the conventional 20μm in order to increase long term stability,[14] while cells fabricated by chemical spraying have used 2μm CdS films due to higher density.[13] Space applications have generally specified transparent or partially transparent coated plastic substrates for flexibility, low weight, and optical transparency, while terrestrial applications usually specify more rigid substrates for mechanical stability. Where weight is not a concern, glass or metal foils have been used as substrates. A variety of such materials exists for construction of both front and back illuminated devices. Initial work proposed here will center on glass, although other materials may be considered for specialized applications.

It is not our intent in this proposal to investigate electrical contacts in detail. However, some effort will be made to <u>survey details of work on contact materials and techniques</u> in order to select materials appropriate to our fabrication and testing requirements. Some possibilities for back illuminated diodes requiring a transparent electrically conducting back surface electrode include SnO_x, $In_xSn_{2-x}O_y$ and Cd_2SnO_4 have been used. Opaque back contacts of

zinc-coated copper, zinc-coated silver-loaded varnishes, and gold-chromium metallizations are possibilities for front illuminated diodes.

The selected contact scheme will be integrated into a research and development program for the fabrication of $CdS-Cu_2S$ photovoltaic cells using the results of earlier experiments on CdS and Cu_xS. The final task will be the testing and evaluation of cells, including accelerated life tests, stress testing, standard spectral response, and electrical load experiments.

Additional Comments

The second area covered by this proposal is the utilization of the extensive analytical capabilities at Sandia Laboratories in the evaluation and characterization of solar cell materials and devices. These analytical capabilities are among the most extensive in the world and have been assembled as a result of work in related areas. The applicable capabilities are summarized below.

1. Physical and Chemical Characterization Facilities

The Chemistry and Materials Characterization Department has the function of supporting the overall research and development effort at Sandia Laboratories. A complete list of capabilities is shown in Table 2. The capabilities and facilities which are most applicable to this proposal are described below. Each instrument or area of characterizations is directed by a Member of the Technical Staff (MTS) who has considerable experience in the particular field. Some of the publications of related work on this equipment are listed in section H.

a. Scanning electron microscopy (SEM) - useful for distinguishing the general grain growth pattern, grain sizes, and surface roughness of the films.

b. Quantiment - a computer-controlled automated, microscopic determination of grain shape and size distributions.

c. Transmission Electron Microscopy (TEM) - would facilitate investigations of grain size (using preferential etching), film porosity, and the general surface morphology.

d. X-ray and Electron Diffraction Analysis - these measurements will establish the crystallographic orientations of the grains.

e. Optical Measurements, Ellipsometry, etc. - these techniques yield the real and imaginary parts of the dielectric constants of transparent films.

f. Trace Chemical Analysis of the Films - this will be necessary to verify doping levels and to search for any impurities introduced during processing. Techniques available include:

   1. Quantitative Wet Chemical Analysis
   2. Neutron Activation Analysis
   3. Atomic Absorption Spectrometry

g. Compositional analysis near the interfaces between films. As a check on the extent of diffusion and compound formation at interfaces the following analysis methods should prove extremely useful:

   1. Auger analysis, combined with ion sputter etching
   2. Ion backscattering spectroscopy
   3. Electron microprobe
   4. Rutherford backscattering

   All of these techniques are capable of giving accurate composition-depth profiles under certain conditions.

TABLE 2

SANDIA LABORATORIES
PHYSICAL AND CHEMICAL
ANALYTICAL TECHNIQUES

Solution Methods:

- Gravimetry
- Titrimetry
- Coulometry
- Ion-selective Electrodes
- Polarography
- Adsorption Spectrophotometry
- Atomic Absorption Spectrometry

Direct Analytical Methods:

- Infrared Spectroscopy
- Gas Chromatography
- Neutron Activation Analysis
- Vacuum Fusion - Mass Spectrometry
- X-ray Fluorescence
- SEM-Energy Dispersive
- Electron Microprobe
- Ion Scattering Spectrometry
- Ion Backscattering Spectroscopy
- Secondary Ion Mass Spectrometry
- Appearance Potential Spectroscopy
- Auger Electron Spectroscopy
- Emission Spectroscopy
- X-ray Diffraction
- Nuclear Reaction Spectroscopy
- Ion Induced X-ray Spectroscopy

Structure/Morphology Analytical Methods:

- X-ray Diffraction
  - Powder
  - Laue
  - Lang
  - Pole Figure
- Scanning Electron Microscopy
- Optical Microscopy
- Transmission Electron Diffraction
- Quantimet (Quantitative Metallography)

Spatial Distribution Methods:

- Ion Scattering Spectroscopy
- Secondary Ion Mass Spectroscopy
- Sputter-Auger Electron Spectroscopy
- Electron Microprobe
- Transmission Electron Microscopy
- Ion Backscattering Spectroscopy

2. Electrical Characterization Facilities

Extensive capabilities exist for the characteristic electrical measurements associated with a solar cell evaluation program. These include:

1. Electrical Resistivity - Several 4 probe resistivity set ups are available for this program. The first, basically a research facility, is capable of measuring 4 probe resistivities from $\sim 10^{+2}$ to 10^{+12} Ω-cm from 1.1 K to 400 K. The other two set ups are designed to characterize materials with somewhat lower resistivities; one of these is a "portable," spring loaded, 4 pin apparatus designed for quick, room temperature characterization as well as material inhomogeniety checks. The other is capable of measurements of samples in vacuum or inert gas up to 1100°C. All these facilities utilize the latest state of the art FET input, digital, electrometers for current and voltage measurements, and in some cases the data is stored and analyzed with a PDP 8 "on-line" computer.
2. Mobility - Two Hall mobility setups are available for use in this program for determinations of carrier number and mobility. The first is a room temperature "characterization" facility interfaced with a PDP 8 computer. The second is a research facility operable over the range 1.1 to 400 K with an extremely high sensitivity ($\sim 5 \times 10^{-3}$ $\frac{cm^2}{v \cdot sec}$). This later apparatus can be extended to higher temperature operation (up to 400°C) with some minor modifications.
3. Seebeck Coefficient - Also useful as an analysis method are measurements of the Seebeck coefficient. These permit determination of the carrier number and scattering mechanisms. Several types of equipment are available. The first apparatus is designed for

fast, low noise, measurements on bulk samples whose impedance can be as high as 10^{11} Ω; this equipment is also usable for thin film measurements with a few modifications. Other apparatus includes a quick, room temperature, portable, Seebeck probe and an ion pumped facility capable of Seebeck measurements from 76 K to ~ 1400 K. This latter apparatus is also interfaced with a PDP 8 computer for rapid data acquisition and analysis.

4. Minority Carrier Lifetime - Several standard methods will be cross-correlated and the lifetime at various illumination intensities will be ascertained.

5. Current-Voltage and Capacitance-Voltage Measurements - In order to probe the nature of electrode-film interfaces, grain boundary barrier regions, and the cell p-n junction itself, current-voltage and capacitance-voltage plots are invaluable. Equipment for performing these experiments includes an automated I-V spectrometer capable of taking accurate I-V plots as well as dI/dV versus V and d^2I/dV^2 versus V. All the data from this apparatus is capable of being "on-line" computer processed and analyzed. Capacitance-voltage data will be obtained using either a General Radio 1615 capacitance bridge with a P.A.R. dual phase lock-in amplifier, or a newly acquired, automatic, digital, Boonton C-V bridge.

6. Measurements of Cell Efficiency - Measurements of cell efficiency as a function of illumination and temperature will be implemented using both indoor Xenon lamps and actual sunlight conditions. Equipment for this phase of the program includes FET input-electrometers for current and voltage measurements--these being interfaced with the PDP 8 computer.

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D. MANAGEMENT PLAN

The tasks to be performed in this CdS/Cu_2S heterojunction solar cell program are presented below. A milestone schedule indicating important decision points is also presented in Figure 3.

Program Management

George Samara, Manager of the Physics of Solids Research Department, is to be the program manager. The program manager will be responsible for program direction, coordination and control of costs and schedules. Status reports, topical reports and the documentation will be proposed or controlled by the program manager. A block diagram of the program organization is presented in Figure 4.

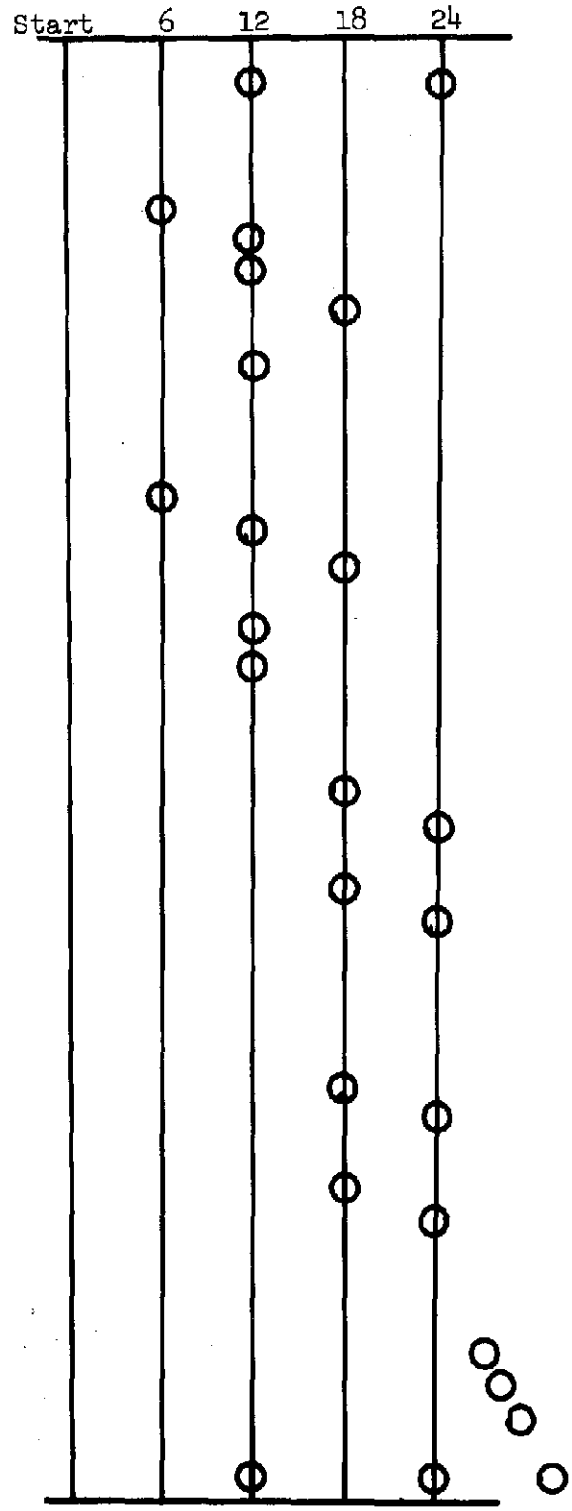
Donald M. Mattox, Supervisor of the Surface Metallurgy Division, is to be the principal investigator. This division has had extensive involvement with thin film physics and technology. Other organizations which will have extensive involvement are the Electrical Transport Division (involved with transport phenomena), Solid State Electronics Division (involved with device development and analysis), Ion-Solid Interactions Division (extensively involved with Rutherford backscattering experiments), and the Materials Analysis Division (involved with scanning electron microscopy, transmission electron microscopy, electron and X-ray diffraction, microprobe, ion backscattering, and other techniques). The capabilities of the laboratory are summarized more extensively in Section C. The pyramidal organizational structure at Sandia Laboratories is designed to encourage intergroup cooperative work on projects such as this.

Task 1 - Properties of CIP CdS

This task consists of the development of a system for the Chemical Ion Plating of CdS and the characterization of CIP films. The principle system variables to be studied are system geometries, evaporation rate effects, discharge voltage, and

Figure 3

MILESTONE SCHEDULE



Program Management

Task 1. CIP CdS

- Fabrication
- Morphology
- Density
- Electrochemical Migration and Diffusion
- Electrical Properties

Task 2. CIP Cu_2S

- Fabrication
- Morphology and Stoichiometry
- Phase Composition and Stability
- Optical Properties
- Electrical Properties

Task 3. Doping of CdS

a. Electrically Active-Fabrication
   Electrical Properties

b. Chemically Active-Fabrication
   Electrochemical and Diffusion Properties

Task 4. Doping of Cu_2S

a. Electrically Active-Fabrication
   Electrical Properties

b. Metallurgically Active-Fabrication
   Stability Studies

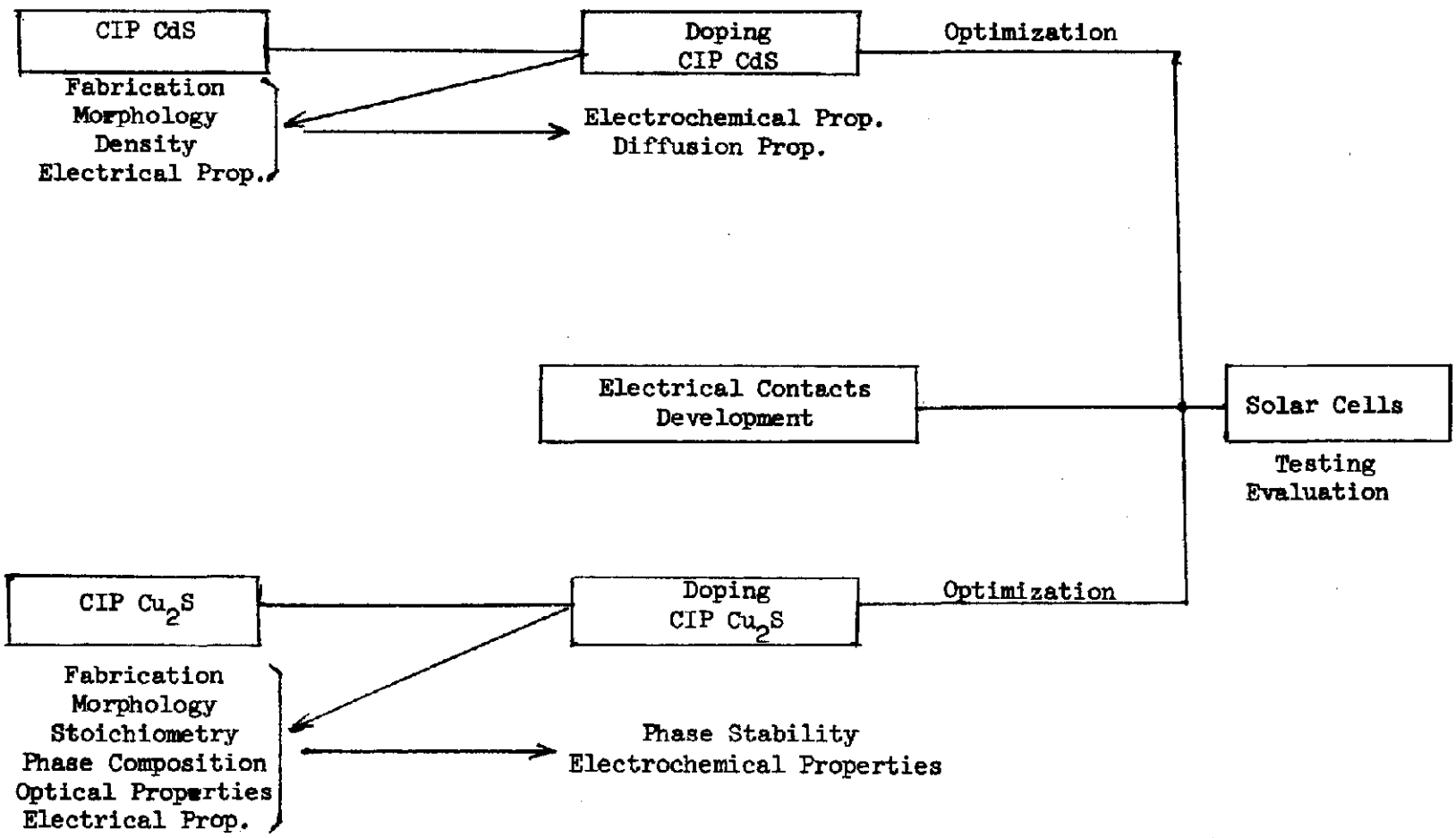
Task 5. Fabrication of CdS-Cu_2S Cells

- Selection of Contact Materials
- Deposition of Cells
- Testing and Evaluation

Decision Points

Figure 4

RESEARCH PLAN



substrate bias and temperature. Fabrication and technology studies will be performed by R. S. Berg (Surface Metallurgy Division). The film properties that are most important are:

1. Film morphology, including crystallite size distribution, fiber axis dispersion, and their uniformity.
2. Film density.
3. Electrical properties transverse and normal to the film, including resistivity, mobility, carrier lifetime, and carrier density.

The morphology analysis will be carried out by the Materials Analysis Division using a variety of techniques. Studies on the diffusion of copper in CdS will be done by J. A. Borders (Ion Solid Interactions Division) using Rutherford back-scattering and by the Materials Analysis Division using ion scattering spectrometry. The electrical studies will be performed by R. D. Nasby (Electrical Transport Division). The task is designed to determine optimum parameters for film densification and the controllability and reproducibility of deposition conditions and electrical properties.

Task 2 - Properties of CIP Cu_2S

This task consists of a developmental program parallel to Task 1 on Cu_2S. The principle system parameters are the same. However, the most important film properties are somewhat different. They are:

1. Phase diagram (stoichiometry and crystallography) and the development of a relatively simple laboratory test to determine composition.
2. Morphology and uniformity.
3. Electrical properties, including resistivity, mobility, lifetime, and carrier densities.

4. Stability and redox reactions resulting from optical, thermal and chemical stimulus.

5. Optical properties (emissivity and absorptivity).

Work on parts 1 and 2 will be performed cooperatively by R. S. Berg and the Solid State Electronics Division. Electrical property studies will be performed by R. D. Nasby (Electrical Transport Division). Stability and optical properties measurements will be performed by the Materials Analysis Divisions and by R. K. Quinn (Solid State Materials Division).

Task 3 - Doping of CIP CdS

This task consists of the characterization of the electrical and chemical properties of CdS films produced by introducing dopants into the films by the CIP process. Since the CIP technique permits much more versatility in selection of dopants than other techniques, it is anticipated that a number of new dopants will be investigated. The dopants are intended to perform the following functions: (1) regulate the electrical properties (resistivity, mobility, lifetime, carrier density, etc.), and (2) control the effects of diffusion of copper in CdS. Studies will also be carried out to determine the effects, if any, of the dopants on the stability, density, morphology, etc., as studied in Task 1. These studies will be carried out by R. S. Berg and R. D. Nasby, together with a variety of analytical groups including the Materials Analysis Division, Ion-Solid Interactions Division, and others.

Task 4 - Doping of CIP Cu_2S

This task parallels Task 3, and consists of the characterization of the effects of dopants on the electrical and metallurgical properties of Cu_2S. The principle function of dopants in Cu_2S are to control the resistivity and stabilize the phase

structure. In conjunction with this, it is important to determine the effects of doping on the other properties of Cu_2S. This task will be done by the same personnel as Task 3.

Task 5 - Fabrication of CdS/Cu_2S Solar Cells

This task consists of several subtasks, including surveys of previous work in contact materials and the fabrication and evaluation of cells produced using the materials techniques developed in Tasks 1-4. Both front and back contact cells will be considered. This will be coordinated by D. M. Mattox. Fabrication techniques will be under the direction of R. S. Berg. An extensive effort will be made to characterize the junction by a variety of techniques. These will include profiling studies, performed by J. A. Borders and the Materials Analysis Division, junction capacitance studies, performed by R. D. Nasby, and load-degradation studies, performed in cooperation with the Solar Energy Projects and Systems Divisions.

Decision Points

In the first 12 months of the study sufficient information should be generated on the effect of the CIP deposition technology on the properties of the CdS and Cu_2S film to determine whether or not the approach has merit. If practical high density CdS films and stoichiometric Cu_2S films can be produced, then the second phase of the program can be funded to tailor and optimize the properties for use in a solar cell configuration.

Since the analytical and standard evaluation techniques developed for use with our program would be applicable to any CdS/Cu_2S program, we propose to make our capabilities available to other investigators. This will entail developing a rapport with other investigators and a mutual appreciation of the problems of fabrication and analysis.

E. RELATED PROGRAMS AND ACTIVITIES WITHIN THE LABORATORIES

The major activities at Sandia Laboratories involve the research, development, design and testing of the non-nuclear portion of nuclear weapons systems. A prime concern in this work is the reliability of components and systems. This requirement has led to extensive high-technology development programs and to in-depth programs in solid state theory, electronic component testing, and degradation simulation. In particular, the Surface Metallurgy Division (D. M. Mattox, supervisor) has a long history in research and development in thin films; the Electronic Technology Department (C. M. Tapp, manager) has extensive experience in transferring thin film component technologies to production facilities; the Solid State Electronic Division (D. G. Schueler, supervisor) in solid state components research and development; Electrical Transport Division (R. T. Johnson, supervisor) in electrical properties; and the Ion-Solid Interactions Division (S. T. Picraux, supervisor) in radiation damage in semiconductors and diffusion studies using Rutherford Backscattering analysis. A very extensive materials characterization department supports these efforts.

Sandia Laboratories has a very active solar-thermal program concerned with collecting energy in the form of heat for utilization in heating, cooling, and electric power generation. Sandia proposed the "total energy concept" where collected thermal energy would be used for electrical power generation and the waste heat would be used for other community requirements. Current programs are in the development and utilization of parabolic focused and central "power tower" collectors. Groups involved in this work include the Solar Energy Projects Division (R. H. Braasch, supervisor), Solar Energy Systems Division (R. P. Stromberg, supervisor), and the Plowshare Technology Division (A. C. Skinrood, supervisor). These groups are supported by the Materials and Process Directorate (L. M. Berry, director).

Sandia also has an in-house photovoltaics program aimed at (1) ascertaining sources of degradation and improving overall cell efficiency of thin film cells, especially CdS/Cu_2S, (2) a scheme for solar photovoltaic-solar thermal integration, and (3) solar cell modeling and parameters studies at room and elevated temperatures using the Sandia Device Simulation Computer Code.

Section H lists some publications in work related to the proposed photovoltaic program.

F. RELATED PROGRAMS IN OTHER ORGANIZATIONS

Mr. J. Jordan of Quantrol, Inc. has been actively pursuing the use of chemical spray techniques; however, Quantrol has relatively little analytical back-up in this effort. By doping the chemical spray, the properties of the CdS can be modified in what is claimed to be a controlled manner. The Cu_2S layer can also be formed by spray techniques. Conceptually, this approach is amenable to high volume production but may suffer from the problem of energy economics since the substrates must be maintained at a high temperature for an appreciable length of time. One aspect of our proposal is the initiation of a cooperative analytical program, in which Sandia's analytical capabilities would be avialable to other investigators. Some initial contacts with Mr. Jordan have been made.

Vacuum deposition-ion exchange techniques are the most conventional approach to the fabrication of CdS-Cu_2S cells. Dr. K. Boer of the University of Delaware is a principal U.S. investigator in this field. This approach is also used by the French in their production effort. Vacuum deposition processes are difficult to control, particularly the vacuum deposition of compounds. No yield or quality data on their cells has been published. Other organizations are studying the use of materials other than CdS and Cu_2S in the heterojunction. It is proposed that the use of other materials can circumvent some of the degradation problems encountered in the CdS/Cu_2S system.

Most of the NSF/RANN grantees and those seeking grants seem to have a rather limited technological and analytical back-up. As part of this proposal we would like to consider the possibility of making our technological, analytical and testing facilities available to others working in this area. This would have the effect of providing them with facilities and capabilities which they do not now possess and in addition, a common testing and evaluation program could be developed

to allow meaningful comparison to be made between devices fabricated by the various techniques from various investigations.

Since our proposed fabrication technique is unique among CdS-Cu_2S investigations, there can be no direct comparison made with the programs. From the standpoint of Thin Film Technology, it is expected that this fabrication technique will be less process sensitive than are the vacuum deposition techniques.

G. UTILIZATION

The use of large area CdS/Cu_2S photovoltaic arrays for electrical power generation is a concept which has been widely discussed in the literature. The feasibility of this concept depends on the economics associated with production, installation, maintenance, and cell lifetime. The technology needed for high volume fabrication of large area thin film systems is well developed* and the thin film industry needs data on the economic aspects of this program in order to make decisions on whether or not to become involved.

The object of this program is to systematically develop the technology needed to fabricate CdS/Cu_2S thin film photovoltaic devices which may be made reproducible, with high yield, high efficiency and with long usable lifetime. By understanding and controlling the individual steps in fabrication it is expected that the information necessary for technology transfer will be generated and the data necessary for economic evaluation will be provided to the thin film industry through publication and presentation of results.

Sandia Laboratories will be available for active participation in the technology transfer to organizations interested in scaling up the process to high-volume production. Such technology transfer to production agencies has been an important function in Sandia's activity for the past 25 years.

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*For example, LOF has been producing 8×10^6 ft.^{2} per year of decorative glass (10' x 12') using 2-layer thin film coatings.

H. PERSONNEL AND BIBLIOGRAPHICS

Sandia Laboratories' experience in program management associated with the research, design, and development of nuclear ordnance provides the basis for the approach used in this proposal. The key personnel involved in major parts of the program have been identified, and their resumes follow. In addition, several other organizations will be involved with specific aspects of the program. Rather than identify all of the numerous personnel that might contribute, bibliographies have been prepared which show the breadth and depth of the capabilities at Sandia Laboratories in several key areas. These bibliographies are not intended to be complete, but are only illustrative of the capabilities at Sandia

NAME: George A. Samara, Program Manager

Education

B.S. - Chemical Engineering, University of Oklahoma, 1958

PhD - Chemical Engineering/Physics, University of Illinois, 1962

Employment Background

Sandia Laboratories: 1962-1963, Staff Member, Applied Physics Research Department

U.S. Army Electronics Laboratories: 1963-1965, Project Officer, Institute for Exploratory Research (Solid State)

Sandia Laboratories: 1965-1967, Staff Member, Physical Research Department; 1967-1971, Supervisor, Solid State Research Division; 1971-Present, Manager, Physics of Solids Research Department

Honors

- Winner 1974 Ipatieff Prize, American Chemical Society
- Chairman 1974 Gordon Conference - Research at High Pressure
- Army Commendation Medal (1965) for outstanding service (Research)
- University of Illinois Fellow 1958-1959
- University of Oklahoma Honors Graduate

Research Interests

- Electronic Structure: Electrical Transport and Insulator and Semiconductor to-Metal Transitions
- Dielectric and Ferroelectric Properties
- Ferromagnetic Properties
- High Pressure Phenomena

Publications

Over 60 publications in the technical literature plus a number of Sandia Reports. The following is a partial list.

"Temperature and Pressure Dependence of the Dielectric Properties of Ionic Crystals and the Properties of Soft Mode Ferroelectrics," in the volume "Materials Under Pressure" of the Honda Memorial Series on Materials Science (to be published 1974).

"Pressure and Temperature Dependences of the Dielectric and Ultrasonic Properties of Polychlorotrifluoroethylene (PCTFE)," with I. J. Fritz, J. Polymer Sci. Letters, Accepted (1974).

"Solar Energy: Sandia's Photovoltaic Research Program," with D. G. Schueler, Sandia Report SLA-74-0281, May 1974.

"Solar Energy: Photovoltaic Conversion for Terrestrial Applications," Sandia Report SLA-74-0280, August 1973.

"Pressure and Temperature Dependences of the Dielectric Properties and Raman Spectra of RbH_2PO_4," with P. S. Peercy, Phys. Rev. B8, 2033 (1973).

"Anharmonic Effects in $KTaO_3$: Ferroelectric Mode, Thermal Expansion and Compressibility," with B. Morosin, Phys. Rev. B8, 1256 (1973).

"Ferromagnetic Materials, Dynamic High Pressure Applications, Dielectric and Ferroelectric Materials and Applications, and High Pressure Sintering," Four Chapters in a Report of the National Academy of Sciences/Materials Advisory Board Committee on High Pressure Technology (NMAB Report-303, January 1973).

"The Grüneisen Parameter of the Soft Ferroelectric Mode in the Cubic Perovskites," Ferroelectrics 2, 177 (1971).

"Effects of Pressure on the Magnetization of Ferrites: Anomalies Due to Strain-Induced Anisotropy in Porous Samples," with R. C. Wayne and R. A. Lefever, J. Appl. Phys. 41, 633 (1970).

"The Effects of Hydrostatic Pressure on Ferroelectric Properties," Chap. 3, pp. 155-239, in Advances in High Pressure Research, Vol. III, R. S. Bradley, Ed., Academic Press (London) 1969.

"Effect of Pressure on the Metal-Non-Metal Transition and Conductivity of Fe_3O_4," Phys. Rev. Letters 21, 795 (1968).

"Temperature and Pressure Dependence of the Dielectric Constants of the Thallous Halides," Phys. Rev. 165, 959 (1968).

"Insulator-to-Metal Transition at High Pressure," J. of Geophysical Research 72, 671 (1967).

"The Compressibility and Electrical Conductivity of Cadmium Sulfide at High Pressures," with A. A. Giardini, Phys. Rev. 140, A 388 (1965).

Publications (Cont'd)

"Temperature Coefficient of Resistance of the High Pressure Phases of Si, Ge, and Some III-V and II-VI Compounds," with S. Minomura and H. G. Drickamer, J. Appl. Phys. 33, 3196 (1962).

"The Effects of Pressure on the Electronic Structure and Conductivity of Insulators and Semiconductors," PhD Thesis, University of Illinois (1962).

"Pressure Induced Phase Transitions in Some II-VI Compounds," with H. G. Drickamer, J. Phys. Chem. Solids 23, 457 (1961).

NAME: Donald M. Mattox, Principal Investigator

Education

B.S. - Eastern Kentucky State University (Physics) 1953

Graduate work - Massachusetts Institute of Technology (Meteorology - USAF) 1953-54

M.S. - University of Kentucky (Physics) 1960

Employment Background

1973-Present

Supervisor, Sandia Laboratories, Surface Metallurgy Division--Supervised approximately 10 persons involved in: Thin film technology development (sputtering, vacuum evaporation, ion plating), fabrication of thin film photovoltaic materials by Chemical Ion Plating, surface-to-surface contact studies (friction and electrical contacts), surface cleaning studies (sputter-cleaning, UV/O_3-cleaning and plasma cleaning), development of selective solar absorber coatings (electrodeposition, vacuum evaporated and gas evaporated), chemical vapor deposition (wear resistant coatings and superconductor materials), hydrogen diffusion in metals (surface properties, diffusion properties, thermal desorption studies).

1969-73

Supervisor, Sandia Laboratories, Surface Physics and Chemistry Division--Supervised approximately 10 persons involved in: Thin film technology development (sputter-deposition, vacuum evaporation, ion plating), surface analysis research and development (Auger spectroscopy, appearance potential spectroscopy), organic adhesives (engineering data generation) effects of ion bombardment on film properties (gas incorporation, morphological changes), thin film metallization, physics of gas discharges as related to sputtering.

1966-69

Supervisor, Sandia Laboratories, Ceramics and Thin Films Division--Supervised approximately 10 persons involved in: Thermodynamics of surfaces, thin film deposition technology, electrical properties of rare earth hydrides, ceramic-to-metal seals, strength and fracture of ceramic materials, chemical vapor deposition of ceramics (boron nitride), thin film metallization (composite film metallization, direct gold metallization of oxides).

1961-66

Staff Member, Sandia Laboratories--Involved in thin film technology development (invented ion plating process), adhesion of thin films, electrical properties of semiconductor materials.

1957-61

Graduate research assistant and instructor--University of Kentucky

1953-57

Lieutenant USAF--Meteorologist

Honors and Professional Activities:

Sigma Xi - 1953
American Vacuum Society
American Physical Society
Board Member--Thin Film Division of American Vacuum Society 1971-present
Chairman Program Committee (Thin Film Division) 21st National Meeting, American Vacuum Society, Anaheim, California, October 1974
Member Program Committee--22nd National Meeting, American Vacuum Society - to be held in Philadelphia, October 1975.
Instructor--American Vacuum Society, Sputtering and Ion Plating Technology Short Course (presented at National Meetings) 1972-73

Publications

"Deposition of Semiconductor Films with High Solar Absorptivity" to be published J. Vac. Sci. Technol.

"Ion Plating - A Review and Update," Proceedings of 6th International Conference on Electron and Ion Beam Science and Technology," to be published.

"Recent Advances in Ion Plating" to be published in Jpn. J. Appl. Phys.

"Effect of Ion Bombardment During Deposition on Thick Metal and Ceramic Deposits: J. Vac. Sci. Technol. 11, 671 (1974).

"High Absorptivity Solar Absorbing Coatings" J. Vac. Sci. Technol. 11, 793 (1974).

"Surface Cleaning by Ultraviolet Radiation" J. Vac. Sci. Technol. 11, 474 (1974).

"The Role of Surface Cleanliness on the Properties of Films Deposited by Ion Plating Techniques" Proceedings of the 1973 International Conference on Sputtering and Its Applications (The French Vacuum Society, Volume des Comptes Rendus, 1er Colloque International de Pulverisation Cathodique et ses Applications-C.I.P. 73, Montpellier, France, 2-5 Octobre, 1973), p. 359 Societe Francaise du Vide, 19, rue du Renard 75004 Paris (F).

"Incorporation and Behavior of Helium in Sputter-Deposited Films" Proceedings of the 20th National Vacuum Symposium of the American Vacuum Society, J. Vac. Sci. Technol. 11, 52 (1974).

"Thin Film Metallization of Oxides in Microelectronics," Thin Solid Films 18, 173 (1973).

"Deposition of Metal Films by Laser-Controlled CVD," Proceedings of the 4th International Conference on Chemical Vapor Deposition, Edited by G. G. Wakefield and J. M. Blocher, Jr. (Electrochemical Society, 1973), p. 196.

"Sputter Deposition and Ion Plating Technology," AVS Thin Film Division Monograph (1973).

"Fundamentals of Ion Plating," Special Proceedings Issue of the 19th National Vacuum Symposium, American Vacuum Society, J. Vac. Sci. Technol. 10, 47 (1973)

"Physical Properties of Thick Sputter-Deposited Glass Films," J. Electrochem. Soc., 120, 1535 (1973).

"Structure Modification by Ion Bombardment During Deposition," J. Vac. Sci. Technol. 9, 528 (1972).

"Incorporation of Helium in Deposited Gold Films," J. Vac. Sci. Technol. 8, 194 (1971).

"Composite Film Metallizing for Ceramics," J. Electrochem. Soc. 117, #11, 1461 (1970).

And 38 other publications dealing with thin film research and development and surface science.

Presentations

"Clean Surface Technology," (Invited) Gordon Research Conference on Adhesion, August 1974.

"Recent Advances in Ion Plating," (Invited), 6th International Vacuum Congress, Kyoto, Japan, March 1974.

"The Role of Surface Cleanliness on the Properties of Films Deposited by Ion Plating Techniques",(Invited), 1973 International Conference on Sputtering and Its Applications, Sponsored by the French Vacuum Society, Montpellier, France, October 1973.

"Thin Film Metallization of Oxides," (Invited), 27th Annual Frequency Control Symposium, Sponsored by the U.S. Army Electronics Command, Cherry Hill, New Jersey, June 1973.

"Ion Plating - Concepts and Applications," (Invited), NASA Technology Utilization Conference on Sputtering and Ion Plating, Cleveland, Ohio, March 1972.

And many other presentations at professional society meetings, industrial and academic locations.

Patent Disclosures

"A Method for In-Situ Formation of Diffusion Barriers During Vapor Deposition of Non-Reactive Metals" (1974).

"A Method of Hydrogen Containment in Metals Through Surface Adsorption of a Polar Molecule Barrier", October 1973.

"A Method for Monitoring the Diffusion of Hydrogen into the Surface of Metals", September 1973.

"A Storage Device for Removing from and Preventing Recontamination of Metallic Surfaces by Oxidizable Contaminants", September 1973.

"Stabilization of Tantalum Nitride Resistors", August 1973.

"Atmospheric Pollution Detector", June 1973

And others

NAME: Raymond S. Berg

Education

B.S. - Electrical Engineering, Purdue University, 1964

M.S. - Electrical Engineering, Purdue University, 1966

PhD - Purdue University, 1972

Employment Background

1972-Present

Member of the Technical Staff, Sandia Laboratories. Involved with deposition techniques, control and modification of morphology; incorporation of gases into materials; transmission electron microscopy.

1967-71

Graduate Instructor in Electrical Engineering, Purdue University.

1960-64

Industry-University Cooperative Student, Automatic Electric Laboratories, Northlake, Ill.

Honors and Professional Activities

NDEA-IV Fellow, 1964-67
Tau Beta Pi Engineering Society
Sigma Pi Sigma Physics Society
Sigma Xi
Institute of Electrical and Electronic Engineers
Electron Microscopy Society of America
American Vacuum Society
Education Committee of the American Vacuum Society
Program Chairman, 11th Annual Symposium, New Mexico Chapter, American Vacuum Society

Publications

"Deposition of CdS by Evaporation Through a Gas Discharge"(w/R. D. Nasby), Proceedings of the 21st National Vacuum Symposium, J. Vac. Sci. Technol., to be published.

"Incorporation and Behavior of Helium in Sputter-Deposited Films", (w/G. J. Kominiak and D. M. Mattox), Proceedings of 20th National Vacuum Symposium, J. Vac. Sci. Technol. 11, pp. 52-55 (1974).

"Deposition of Metal Films By Laser-Controlled CVD", (w/D. M. Mattox), Proceedings of the 4th International Conference on Chemical Vapor Deposition, The Electrochemical Society, Princeton, N.J. (1973).

"Deposition of Metal Films by Laser-Controlled CVD"(w/D. M. Mattox), Extended Abstract, J. Electrochem. Soc. (August 1973).

"Block Line Interactions in Coarsely Crystalline Permalloy Films", Ph.D. Dissertation, Purdue University (1972).

"A Survey of Non-Ohmic Phenomena in Materials", Automatic Electric Laboratories, Inc., Report PD-0110 (1964).

Presentations

"Deposition of CdS by Evaporation Through a Gas Discharge", (w/R. D. Nasby) 21st National Vacuum Symposium, American Vacuum Society, Pasadena, California, October 8-11, 1974.

"Block Line Interactions in Coarsely Crystalline Permalloy Films," (w/ F. J. Friedlaender and L. F. Silva), International Magnetics Conference, Toronto, Canada, May 14-17, 1974.

"Effect of Thin Film Geometry on Helium Incorporated Into Gold Films", (w/G. J. Kominiak and D. M. Mattox), Third Annual Symposium, Florida Chapter of the American Vacuum Society, St. Petersburg, Florida, February 6-7, 1973.

"Incorporation and Behavior of Helium in Sputter-Deposited Films", (w/G. J. Kominiak and D. M. Mattox), 20th National Vacuum Symposium, American Vacuum Society, New York, New York, October 9-13, 1973.

"Deposition of Metal Films by Laser-Controlled CVD", (w/D.M. Mattox), 4th International Conference on Chemical Vapor Deposition, Electrochemical Society, Boston, Massachusetts, October 7-12, 1973.

"Incorporation and Behavior of Helium in Sputter Deposited Films", (w/G. J. Kominiak and D. M. Mattox), Conference on Surface Studies, Dow Chemical Co., Golden, Colorado, September 5-7, 1973.

"Evaluation of Magnetic Films by Lorentz Microscopy," Midwest Section, American Vacuum Society, Argonne National Laboratory, Argonne, Illinois, May 21-22, 1970.

NAME: Robert D. Nasby

Education

B.A. - Physics, Rice University, 1961

M.S. - Physics, Solid State, Purdue University, 1963

PhD. - Physics, Solid State, University of Texas, 1967

Work History

Sandia Laboratories: 1968-present, Staff Member. Research on transport properties of materials with specific areas of: electrical and thermal transport properties of SiGe thermoelectric alloys, precipitation of dopants in SiGe thermoelectric alloys, and the electrical properties of CdS films produced by Chemical Ion Plating.

Texas Instruments Incorporated: Summer Employment, 1960,62,63, and 64. Studied effects of semiconductor processing steps on electrical properties of base silicon slices, reliability studies of a Mariner spacecraft electronic package, reliability production moniter for Ranger spacecraft electronic package, missile feasibility study.

Honors

- Texas Instruments Inc. Fellowship, University of Texas, 1964-1967
- General Electric Foundation Scholarship, Purdue University, 1961-1962
- Member Sigma Pi Sigma
- Who's Who in the West

Publications

"Deposition of CdS by Evaporation Through Gas Discharge," with R. S. Berg, J. Vac. Sci. and Technol., to be published, Jan. 1975.

"Application of the Lifshitz-Slyozov Theory to Precipitation of Phosphorus in Silicon-Germanium Thermoelectric Alloys," with E. L. Burgess, J. Appl. Phys. 45, 2375 (1974).

"Characterization of the Thermoelectric Properties of Silicon-Germanium Alloys," with E. L. Burgess, Sandia Technical Review SLA-73-0651; The MC2730 Radioisotopic Thermoelectric Generator: A Development Report, SLA-74-0046 (1974).

"Room Temperature Electrical Properties and Dopant Precipitation for SiGe Thermoelectric Alloys," with E. L. Burgess, Proc. Seventh Intersociety Energy Conversion Engineering Conference (1972), p. 130.

"Precipitation of Dopants in Silicon-Germanium Thermoelectric Alloys," with E. L. Burgess, J. Appl. Phys. 43, 2908 (1972).

"A Concept for a Chemically Powered Thermoelectric or Thermionic Power Supply," Sandia Laboratories Report SC-RR-70-640 (1971).

"Hall Effect in Lithium-Ammonia Solutions," with J. C. Thompson, J. Chem. Phys. 53, 109 (1970); and in Metal Ammonia Solutions, ed. William L. Jolly, Benchmark Papers in Inorganic Chemistry Series (Dowden-Hutchinson, 1972).

"On Measurement of the Hall Effect in Metal-Ammonia Solutions," with J. C. Thompson, J. Chem. Phys. 49, 969 (1968).

"A Study of the Hall Effect in Metal-Ammonia Solutions in the Metal to Non-Metal Transition Region," PhD Dissertation, University of Texas (1967).

NAME: Rod K. Quinn

Education

B.S. - Chemistry, Southern Methodist University, May 1961

M.S. - Physical Chemistry, Southern Methodist University, August 1963

PhD. - Inorganic Chemistry, University of Texas, June 1967

Employment Background

Sandia Laboratories: June 1967-present. Staff member in materials research division of solid state research department. Duties have included a variety of research problems in electrochemistry, solid state chemistry, and inorganic crystal synthesis. The instruments and techniques adapted to and used in these programs include stationary electrode voltammetry, ring-disk voltammetry, rotating ring-disk cyclic voltammetry, Faraday magnetic susceptibility, quadropole mass spectrometry, differential scanning calorimetry, thermogravimetry, differential thermal analysis, vapor transport-crystal growth, and UV-vis-near IR spectrometry

Texas Instruments Incorporated: (Semiconductor Research and Development Laboratories) June 1960-August 1961. Engineer in charge of coordinating device development for a 1-3 amp power transistor, 2N2150, with particular responsibility for materials and materials compatability problems.

Texas Instruments Incorporated: (Semiconductor Research and Development Laboratories) Summers 1959, 60, 62 and 64. Various responsibilities in materials problems related to semiconductor devices.

Professional Activities and Honors

R. A. Welch Fellowship 1965, 1966, 1967

Member, American Chemical Society

Member, Honorary Society Phi Lambda Upsilon

Member, Honorary Society Sigma Xi

Member, Electrochemical Society

Publications

"Electrochemistry at Thin Solid Films," with N. R. Armstrong and N. E. Vanderbough, J. Vac. Sci. Technol, in press.

"Rotating Ring Disk Electrode Studies of the Electrochemistry of Aromatic Carbonyl Compounds in the Solvent Sulfolane," with N. R. Armstrong and N. E. Vanderbough, J. Electrochem. Soc., in press.

"NMR and Susceptibility Studies of Pt-Rh Alloys," with H. T. Weaver, Phys. Rev., 10, 1816 (1974).

"Compositional Dependence of Structural and Thermal Properties of As-Te Amorphous Alloys," Materials Res. Bull. 9 (6), 803 (1974).

"Surface Nucleated Crystallization in $Ge_{15}Te_{80}As_5$ Semiconducting Galsses," with R. T. Johnson and C. J. Miglionico, Materials Res. Bull. 9 (5), 667 (1974).

"Voltammetry in Sulfolane I: The Electrochemical Behavior of Benzaldehyde and Substituted Benzaldehydes," with N. R. Armstrong and N. E. Vanderborgh, Analytical Chemistry, 46, 1759 (1974).

"Electrical and Structural Properties of Annealed As-Te and As-Te-I Semiconducting Glasses: Surface and Bulk Effects," with R. T. Johnson and J. A. Borders, J. Non-Crystalline Solids, 15, 289 (1974).

"NMR and Susceptibility Studies of Pt-Rh Alloys," with H. T. Weaver, Proceedings of the Nineteenth Annual Conference on Magnetism and Magnetic Materials, 1973, Boston, Mass., 297.

"Spontaneous Generation of Acoustic Signals During Switching of Amorphous Semiconductors," with A. C. Beattie and R. T. Johnson, Jr., Proc. of the Fifth International Conference on Amorphous and Liquid Semiconductors, 1973, Garmisch-Partenkirchen (F.R. Germany), J. Stuke and W. Brenig, eds., Taylor and Francis CTD, London, pp. 881-887.

"Electrical Transport and Structural Properties of Bulk As-Te-I, As-Te-Ge, and As-Te Chalcogenide Glasses," with C. H. Seager and D. Emin, Phys. Rev. B8, 4746 (1973).

"Nuclear Resonance and Magnetic Susceptibility Study of Platinum - Group IV A Compounds," with H. T. Weaver, R. J. Baughman, and R. C. Knauer, J. Chem. Phys., 59, 4961 (1973).

"Magnetic and Structural Properties of Manganese Pyridine Linear Chain Salts," with P. M. Richards and B. Morosin, J. Chem. Phys., 59, 4474 (1974).

"Thermally-Induced Structural and Electrical Effects in Ge-Te-Based Amorphous Alloys," with R. T. Johnson, Jr., J. Non-Crystalline Solids, 12, 213 (1973).

"Preparation, Single Crystal Growth, and Characterization of PtSi and PtGe," with R. J. Baughman, Mater. Res. Bull. 7, 1035 (1972).

"Low Temperature Faraday Susceptibility Apparatus," with R. C. Knauer, Rev. Sci. Instrum. 43, 1543 (1972).

"Thermally Induced Surface and Bulk Electrical Effects in Semiconducting Glasses," with R. T. Johnson, Jr., J. Appl. Phys. 43, 3875 (1972).

"Nuclear Resonance and Susceptibility Studies on PtSi," with H. T. Weaver, R. C. Knauer, and R. J. Baughman, Solid State Communications 11, 453 (1972).

"Small Polaron Hopping Motion in Some Chalcogenide Glasses," with D. Emin and C. H. Seager, Phys. Rev. Letters 28, 813 (1972).

"Electronic Transport Measurements in the As-Te-I Chalcogenide Glasses," with C. H. Seager and D. Emin, J. Non-Crystalline Solids 8-10, 341 (1972).

"Compositional Dependence of the Thermal, Structural, and Electrical Properties of As-Te-I Glasses," with R. T. Johnson, Jr., J. Non-Crystalline Solids 7, 53 (1972).

"Vaporization Associated with Surface Electrical Switching As-Te-I and As-Te-Ge Glasses," with R. T. Johnson, Jr. and D. A. Northrop, Solid State Communications 9, 1397 (1971).

"Electrical Conductivity and Surface Layer Formation in Semiconducting $As_{50}Te_{45}I_5$," with R. T. Johnson, Jr., Solid State Communications 9, 393 (1971).

"The Growth of Rhenium (VI) Oxide Single Crystals by a Vapor Transport Mechanism," with P. G. Neiswander, Materials Res. Bull. 5, (5) 329 (1970).

"Metal-Ammonia Solutions. VII. The Electrolysis of Liquid Ammonia Solutions of Aluminum (III) Iodide and Magnesium (II) Chloride," with J. J. Lagowski, Inorganic Chemistry 9, 414 (1970).

"Metal-Ammonia Solutions. IV. Spectra of Dilute Metal-Ammonia Solutions," with J. J. Lagowski, J. Phys. Chem. 73, 2326 (1969).

"Metal-Ammonia Solutions. III. Spectroscopy of Quaternary Ammonium Radicals," with J. J. Lagowski, J. Phys. Chem. 72, 1374 (1968).

"The Magnetic Susceptibility of Tantalum Diselenide," with R. Simmons and J. J. Banewicz, J. Phys. Chem. 70, 230 (1966).

NAME: Bruno Morosin

Education

University of Oregon, Eugene, Oregon; major: chemistry; minors: physics and math; BA (1956).

University of Washington, Seattle, Washington, Physical Chemistry (x-ray diffraction); Ph.D. (1959).

Employment Background

Sandia Laboratories, 1961 to present; research concerns the relationships of crystalline structure and physical properties, emphasizing anisotropic thermal expansivities, thermodynamic properties of solids, polymorphism and phase transitions, magnetic interactions and chemical bonding; supervisor (1967) Chemical Physics, (1969) Electronic Properties in Solids, (1971) Structural Phenomena in Solids, (1973) Solid State Materials.

Honors and Professional Activities

American Men of Science; served on committees of the American Crystallographic Society; member of American Physical Society; refereed papers for Acta Crystallographica, Physical Review, Inorganic Chemistry, Journal of Applied Physics, Journal of Applied Crystallography, and Journal Chem. Phys. Sol.

Publications

Authored or coauthored over 80; those appearing during 1973 and 1974 are as follows:

"Structure Refinements on Dichloro- and Dibromobis (Pyridine) Copper (II)," Acta Cryst. (at press).

"Structural and EPR Search for Exchange Striction in Pyrazine Copper Acetate," w/R. C. Hughes and Z. G. Soos (Princeton), Acta Cryst. (at press).

"Electron Spin Resonance and Structure of Magnetically Inequivalent Chains in $CuCl_2 \cdot 2NC_5H_5$," w/R. C. Hughes, P. M. Richards, and W. Duffy, Jr. (Santa Clara Univ.), Phys. Rev. (at press).

"Solid Electrolyte Materials," w/R. T. Johnson, SAND74-0296, 10/74.

"Structure Refinement on NbS_2," Acta Cryst. 30 B, 551 (1974).

"Crystal Structure of BIS Benzene Chromium Iodide," Acta Cryst. B 30, 838 (1974).

"Low Temperature, High Pressure X-Ray Cell," w/J. E. Schirber, J. Appl. Cryst 7, 295 (1974).

"Crystal Structures of 2,2',4,4',6,6'-Hexanitroazobenzene (HNAB), Form I and Form II," w/E. J. Graeber, Acta Cryst. 30 B, 301 (1974).

"Pressure-Induced Low-Temperature Transitions in TMMC," w/G. A. Samara and P. S. Peercy, Solid State Commun. 13, 1525 (1973).

"La_2O_2S Structure Refinement and Crystal Field," w/D. J. Newman (Queen Mary College, London), Acta Cryst. B 29, 2647 (1973).

"Magnetic and Structural Properties of Manganese Pyridine Linear Chain Salts," w/P.M. Richards and R. K. Quinn, J. Chem. Phys. 59, 4474 (1973)

"Crystal and Molecular Structure of Thiocyanotobis (Triphenylphosphine) Silver (I)," w/J. Howatson (Univ. of Wyoming), Crystal Structure Comm. 2, 51 (1973).

"Pressure and Temperature Dependences of the Raman Active Phonons in SnO_2," w/P. S. Peercy, Phys. Rev. B7, 2779 (1973).

"Anharmonic Effects in $KTaO_3$: Ferroelectric Mode, Thermal Expansion, and Compressibility," w/G. A. Samara, Phys. Rev. B 8, 1256 (1973).

"Crystal Structure and Linear Thermal Expansivities of Platinum Silicide and Platinum Germanide," w/E. J. Graeber and R. J. Baughman, Acta Cryst. B 29, 1991 (1973).

"Phase Transitions In TMMC and Related Compounds," w/P. S. Peercy and G. A. Samara, Phys. Rev. B 8, 3378 (1973).

"Crystal Structure, Linear and Nonlinear Optical Properties of $Ca(IO_3)_2 \cdot 6H_2O$," w/J. G. Bergman and G. R. Crane, BTL, Acta Crystallographica B 29, 1067 (1973).

NAME: James A. Borders

Education

Reed College (1959-1963)
B.A. in Physics (1963)

University of Illinois
M.S. in Physics (1965)
Ph.D. in Physics (1968)

Employment Background

July, 1969 - Present

Sandia Laboratories
Albuquerque, New Mexico'
Ion-Solid Interactions Division

June 1965-August 1965

Lawrence Radiation Laboratory
Livermore, California

June 1964 - August 1964
June 1962 - August 1962
June 1961 - August 1961

Minnesota Mining & Mfg. Co. Research Laboratories
St. Paul, Minnesota

All unaccounted for time was spent in undergraduate or graduate school

Honors and Professional Organizations

American Physical Society (Solid State Division)
Sigma Xi
American Association of Physics Teachers
The ElectroChemical Society

Publications

"The Formation of Substitutional Alloys by Ion Implantation in Metals," with J. M. Poate, W. J. DeBonte and W. M. Augustyniak, Appl. Phys. Letters. (accepted for publication).

"The Formation of Substitutional Alloys in FCC Metals by High Dose Implantation," with J. M. Poate, Proc. of 4th Intl. Conf. on Ion Implantation in Semiconductors and other Material (to be published).

"Characterization of Silicon Metallization Systems Using Energetic Ion Backscattering," with S. T. Picraux, Special Issue of the Proc. of the IEEE on the Effects and Uses of Energetic Radiation in Electronic Materials 62, 1224 (1974).

"Electrical and Structural Properties of Annealed As-Te and As-Te-I Semi-Conducting Glasses: Surface and Bulk Effects," with R. T. Johnson and R. K. Quinn, J. Non-Crystalline Solids 15, 289 (1974).

"Stopping Power of Cadmium Sulfide for Helium Ions," with P. Engel and F. Chernow, J. Appl. Phys., Vol. 45, 38, 1974.

"Helium Ion Stopping Cross Sections in Bismuth, Lead and Tungsten," Radiation Effects 21, 165 (1974).

"The Application of Helium Ion Backscattering to Electrical Contact Studies for the RTG," SLA 74-0046, titled: The MC2730 Radioisotopic Thermoelectric Generator: A Development Report.

"The Application of Helium Ion Backscattering to Electrical Contact Studies for the RTG," w/J. N. Sweet, Sandia Tech. Rev. SLA-73-0651.

"Ion Backscattering Study of WSi_2 Layer Growth in Sputtered W Contacts on Silicon," with J. N. Sweet, Proc. Intl. Conf. on the Applications of Ion Beams to Metals, Albuquerque, 10/2-4/73.

"Ion Backscattering Analysis of Interdiffusion in Cu-Au Thin Films," Proc. Intl. Conf. on Ion Beam Surface Layer Analysis, Yorktown Heights, N.Y., 6/18-20/73. Thin Solid Films 19, No. 2, pp. 359-370 (1973).

"^{16}O Contamination in ^{4}He Analysis Beams," with S. T. Picraux and R. A. Langley, Proc. Intl. Conf. on Ion Beam Surface Layer Analysis, Yorktown Heights, N.Y., 6/18-20/73. Thin Solid Films 19, No. 2, pp. 371-380 (1973).

"Helium Ion Stopping Cross-Sections in Gold," Radiation Effects 16, 253 (1972).

"Ion-Backscattering Analysis of Tungsten Films on Heavily-Doped SiGe," with J. N. Sweet, J. Appl. Phys. 43, 3803 (1972).

"Oxidation of Scandium," with D. H. Loescher and G. E. Pike, J. Vac. Sci. Technol. 9, 159 (1972) (abstract only).

"Comments on a Simplified Technique for Crystal Alignment During Channeling Effect Measurements," with S. T. Picraux, Review of Scientific Instruments 42, No. 11, 1740 (1971).

"Infrared Studies of SiC, Si_3N_4 and SiO_2 Formation in Ion-Implanted Silicon," Proceedings of the IInd International Conference on Ion Implantation in Semiconductors, Garmisch-Partenkirchen, Germany, May 24-28, 1971, with W. Beezhold, edited by I. Ruge and J. Graul (Springer-Verlag, 1971).

"Formation of SiC in Silicon by Ion Implantation," Appl. Phys. Letters 18, 509 (1971), with S. T. Picraux and W. Beezhold.

"Luminescence From Implanted Zn Ions in GaAs," Radiation Effects 9, 257 (1971), with R. E. Whan, G. W. Arnold, and J. K. Maurin. Proceedings of the Intl. Conf. on Rad. Effects in Semiconductors, Albany, N.Y., August 23-27, 1970.

"Near Band-Edge Optical Absorption Produced by Ion Implantation in GaAs," Appl. Phys. Letters 18, 16 (1971).

"Infrared Studies of the Crystallinity of Ion-Implanted Si," Radiation Effects 6, 19 (1970), with F. L. Vook, D. K. Brice, S. T. Picraux, and H. J. Stein.

"EPR of Substitutional Group V Implants in Silicon," with K. L. Brower, Radiation Effects 6, 135 (1970).

"A Simplified Technique for Crystal Alignment During Channeling Effect Measurements," Rev. of Sci. Instruments 41, 1230 (1970), with S. T. Picraux.

"Conduction Band Symmetry and Spin-Dependent Polaron Transport in the Alkali Halides," with J. W. Hodby and F. C. Brown, J. Phys. C 3, 335 (1970).

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BUDGET*

		First Year	Second Year
A. Salaries and Wages			
Senior Staff	(0.5)	30 K	32 K
Professional Staff	(2.5)	150 K	158 K
Clerical-Technical	(2.0)	70 K	75 K
B. Staff Benefits		0	0
C. TOTAL		250 K	265 K
D. Permanent Equipment		--	--
E. Expendable Equipment and Supplies		25 K	25 K
F. Travel - Domestic		3 K	3 K
G. Publication Costs		2 K	2 K
H. Other Costs (subcontracts, analytical work for other NSF/RANN Grantees)		25 K	50 K
I. TOTAL Costs		305 K	345 K

*Note: Because of existing capabilities, there will be no start-up period or costs.

Senior Staff

D. M. Mattox	50%	

Professional Staff

R. S. Berg	75%	(Fabrication Characterization)
B. Morosin	25%	(Structure Analysis and Stability)
R. D. Nasby	50%	(Electrical Properties)
J. A. Borders	25%	(Diffusion)
R. K. Quinn	25%	(Electrochemical Properties)

Attachment 1

Structure Modification by Ion Bombardment during Deposition*

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(Received 28 July 1971)

It is shown that continuous or intermittent ion bombardment during deposition can change the growth mode of thick deposits formed by sputtering or evaporation. The columnar morphology commonly found when deposits exceed 1 μ in thickness can be disrupted and the deposit densified by negatively biasing the deposit and subjecting it to ion bombardment during growth. This effect is found to occur in a number of metal systems and may be attributed to resputtering during growth. In the case of sputter deposited tantalum, the density of 6-μ thick films can be increased from 14 g/cm^3 at 0 deposit bias to 16.3 g/cm^3 at -500-V bias. The macroscopic stress in the deposited film is also shown to be a function of the deposit bias. It is proposed that this growth habit modification may also be obtained in sputter deposited nonmetallic materials and chemical vapor deposits by ion bombarding the deposit during growth.

Introduction

With the advent of high capacity evaporation and sputtering equipment and techniques, interest in thick deposits of metals and alloys has increased. These thick deposits have been used to form coatings and freestanding shapes such as alloy coatings on gas turbine blades,[1] and titanium foil.[2] Of particular concern are the morphology, density, and adherence of thick deposits formed by sputter deposition and electron beam evaporation. Closely related to the problem of adherence is the stress introduced into the deposits during deposition.[3]

A major problem in the formation of thick deposits is the columnar morphology which usually occurs when the deposit thickness becomes greater than about 1 μ. This growth habit determines many of the physical properties of the deposit. The usual procedure for disrupting the growth of this columnar habit is to deposit the material on a heated substrate, allowing recrystallization and grain growth during deposition.[4] This is effective when depositing relatively low melting elements and alloys, but is not feasible when depositing refractory materials. The columnar morphology obtained when chemically vapor depositing (CVD) tungsten may be disrupted by mechanically disturbing the surface during deposition[5] and the smoothness of tungsten CVD coatings may be increased by ion bombardment of the deposit during growth.[6]

* This work supported by the U. S. Atomic Energy Commission.

It has been proposed that resputtering of films during sputter deposition is an important factor in obtaining good coverage over steps.[7,8] The resputtering tends to fill in growth defects present in the films at steps thus providing a "healing" mechanism. The same effect has been noted in the bias sputter deposition of metal films into slots[9] and in the coverage of surfaces coated by the ion plating process.[10]

Recently it has been reported[11] that copper deposited by high rate sputtering (>100 Å/sec) using krypton exhibits recrystallization and grain growth at room temperature whereas low rate sputter deposits do not. This effect is attributed to a higher stress and defect density in the high rate deposits than is found in the low rate deposits. A substrate bias effect was also noted and is attributed to the reduction of oxygen contamination in the copper deposit with the application of a small negative bias (-75 V). Similar effects have been reported in other bias sputtering studies.[12] Although appreciable gas may be trapped during the sputtering process,[13] little krypton was incorporated into the sputter deposited copper. Trapped gas has been found to affect the grain growth in thin films.[14]

The object of this study was to investigate the effect of deposition techniques and parameters on the morphology and properties of thick deposits (1 to 25 μ) of tantalum. Of interest were techniques capable of disrupting the columnar habit and densifying the deposits.

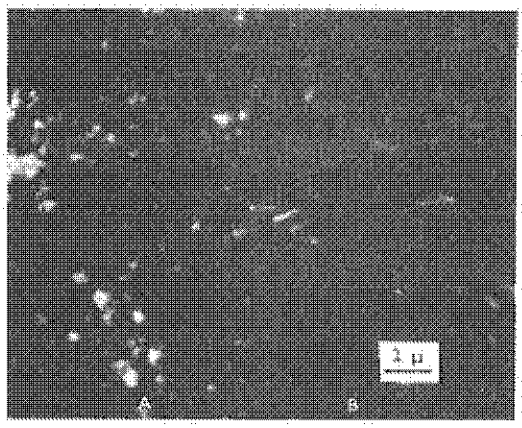

FIGURE 1. Surface of biased (A) and grounded (B) 6-μ thick tantalum deposits. 300°C.

Experimental

A planar dc diode system was used to sputter deposit the tantalum. The tantalum sputtering cathode was water cooled and the 10-mil thick poco graphite[15] or tantalum substrates were clamped to a copper block which could be heated or water cooled during deposition. Typical deposition parameters were 3500-V target potential and 0.3-mA/cm² cathode current density at 35-μ argon gas pressure with a target-substrate separation of 8 cm. These conditions give a deposition rate of about 2.0 mg/cm²/h. The principal deposition variables studied were substrate bias and temperature during deposition.

Results

The most obvious bias-related property of thick deposits is the optical reflectance. The tantalum deposits formed on grounded (0 bias) substrates have a dull matte appearance whose reflectance varies with direction of viewing while those formed with a high (−500 V) negative bias have a shiny, metallic appearance. Figure 1 shows scanning electron microscopy (SEM) pictures of two such surfaces. The matte surface is very rough and looks like a forest of dendrites about 0.5 μ in diameter emerging from the surface. This gives a diffusively reflecting surface. The metallic appearing surface is much smoother giving specular reflection. Figure 2 shows SEM pictures of polished and etched cross sections of the two deposits. The grounded deposit shows a very columnar morphology while the biased deposit shows little evidence of a columnar habit. Figure 3 shows a fracture cross section and surface view of a columnar deposit showing a nodular growth which is sometimes found in the grounded deposits. This type of growth is apparently associated with a surface defect on the substrate. These types of features were not found in the biased deposits.

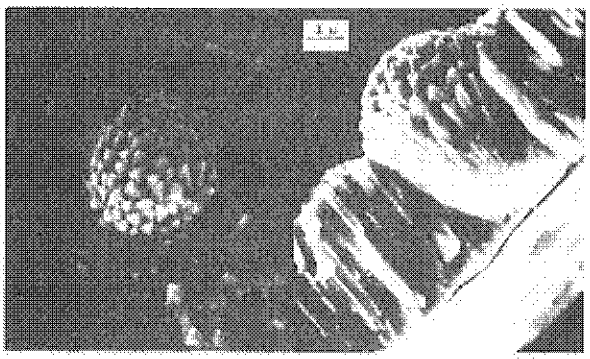

FIGURE 3. Surface and fracture cross-sectional view of nodular growth sometimes found in grounded tantalum deposits.

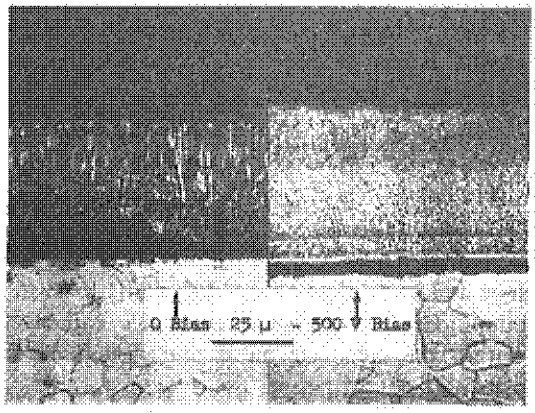

FIGURE 2. Polished and etched cross sections of biased and grounded tantalum deposits.

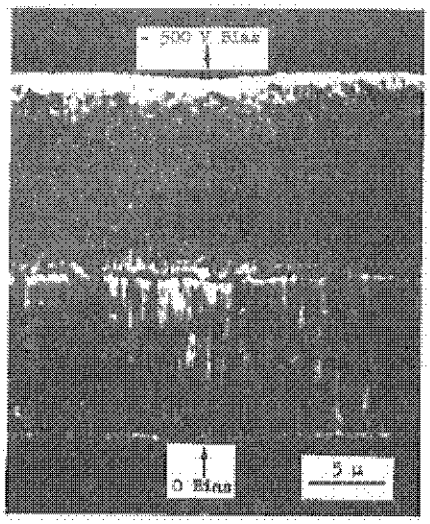

FIGURE 4. Polished and etched cross section of tantalum deposit begun in the grounded condition then changed to a biased condition.

TABLE I. Crystallite size.

Bias (Volts)	Temperature (°C)	Structure	Crystallite size (Å) from D_{110}	Crystallite size (Å) from D_{211}	Note
+200	300	β-Ta+bcc-Ta	364	133	
0	600	β-Ta+bcc-Ta	*	*	
0	300	bcc-Ta	757	207	
-250	300	bcc-Ta	414	140	(200)
-500	300	bcc-Ta	211	63	(200)
-500	600	bcc-Ta	219	61	(200)
					Increasing (200) intensity

* β-Ta peaks too strong to allow bcc crystallite size measurement.

In the case of tantalum under these bias deposition conditions, the visual habit modification of the deposits seems to occur when the substrate bias is greater than 200 V negative. This varies somewhat with substrate temperature in that the columnar morphology is more obvious at the low temperature (~20°C) studied than at the higher temperature (600°C).

It is found that the habit modification can be made to occur at any stage of the deposition. Figure 4 shows a polished and etched tantalum deposit which began growth on a grounded substrate and shows the typical columnar habit. A −500-V bias was then applied and the habit immediately became less columnar. If the bias is shut off, the habit again becomes columnar.

As one would expect, the density of the deposits is related to their morphology and was found to increase with negative substrate bias. Densities were determined by weighing the substrates before and after deposition and measuring the deposit thickness on metallographic sections. Figure 5 shows the density variation obtained on deposits formed on carbon at 300°C as a function of substrate bias. Each point represents an average of at least three samples. The bulk density for tantalum is 16.6 g/cm³.

The relative macroscopic stress in the substrate-deposit system was determined by a cantilever technique often used to determine the stress in electrodeposits.[16] By knowing the dimensions and modulus of the beam and the film material, an absolute value for stress may be calculated. Since one would expect the modulus of the deposit material to vary with habit, we did not determine an absolute value for stress but rather determined the relative stress. This was done by measuring the deflection of 10-mil thick graphite beams and expressing the stress as the sagitta length as measured by a toolmaker's microscope. Typical beams were 3.8-cm long and the modulus of the poco graphite beams was measured to be 10.8×10^{10} dyn/cm².[17] Figure 6 shows the relative stresses measured as a function of substrate bias normalized for slight differences in deposit thickness, beam modulus, and beam length. The more dense deposits formed at high negative bias exhibit the most stress. All sputter-deposited tantalum showed intrinsic compressive stress as has been reported with other sputter deposited metals.[18] At higher substrate biases there was a decrease in deposition rate of up to 20%.

Relative crystallite size was determined using x-ray line broadening techniques. Table I shows the size variation as a function of substrate bias and temperature. The measurement of size was complicated by the presence of β tantalum[19] at ground and positive bias and appearance of the (200) diffraction line at higher biases. Size measurements on two crystallographic

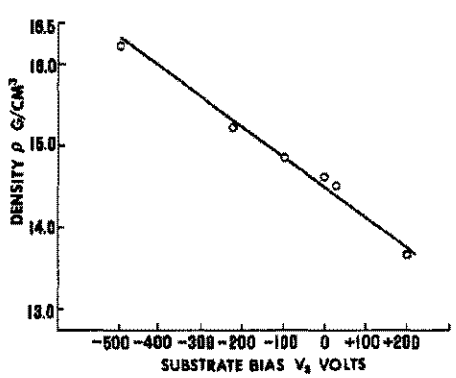

FIGURE 5. Density of 6-μ thick tantalum deposits formed at 300°C as a function of substrate bias during deposition.

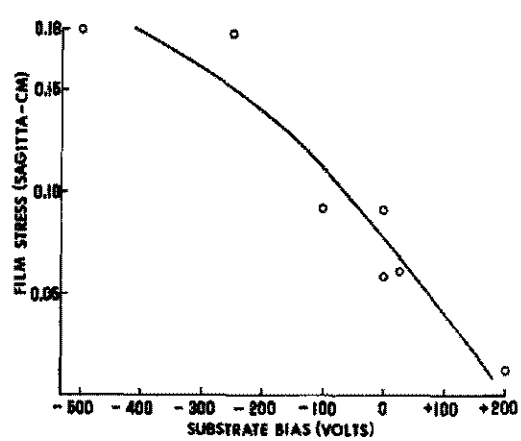

FIGURE 6. Relative stress of 6-μ thick tantalum deposits formed at 300°C as a function of substrate bias during deposition.

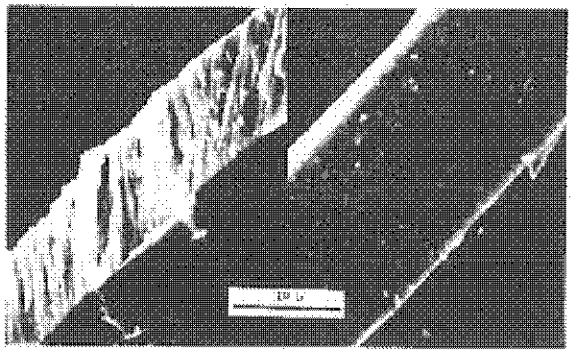

FIGURE 7. Chromium deposits sputter deposited on beryllium without a bias (A) and with a −500-V bias (B). Fracture cross section.

planes indicate that the crystallites are not of a cubic geometry. These facts along with the unknown instrument broadening makes the absolute values of crystallite size in doubt but apparently the trend is to smaller, more randomly oriented crystallites at the higher negative biases. It is of interest to note that the measured size is much smaller than the size of the columns seen by SEM. This would indicate that the columns are composed of a multitude of small crystallites which have preferred orientation.

The technique of habit modification and densification by ion bombardment during growth by sputter deposition has been used in several other systems. Figure 7 shows chromium sputter deposited on beryllium with and without a bias. A much more uniform, dense material is formed with an impressed bias. The adhesion of the deposit was also greatly improved when using the bias during deposition.

Electron beam evaporation also gives a columnar morphology in thick deposits of tantalum. Some habit modification can be accomplished by evaporating at a high rate and negatively biasing the substrate so the deposit is bombarded by metal ions formed above the molten pool of metal. The fracture cross section of a tantalum deposit formed by electron beam evaporation in vacuum at a rate of 15 mg/cm²/h is shown in Fig. 8. The deposit was begun with no bias and shows the typical columnar habit. A bias of −4 kV was then applied and the columnar morphology became less apparent. The substrate current density was about 1 mA/cm² with the bias applied. The evaporated tantalum deposits were found to have tensile stress.

Electron beam evaporated deposits and to some extent sputter deposits show the interesting property of having the axis of the columns in the columnar habit directed toward the source of the vapor. Since the crystallites in the columns have a highly preferred orientation this means that a complex structure can be produced which has a specific crystallographic configuration.

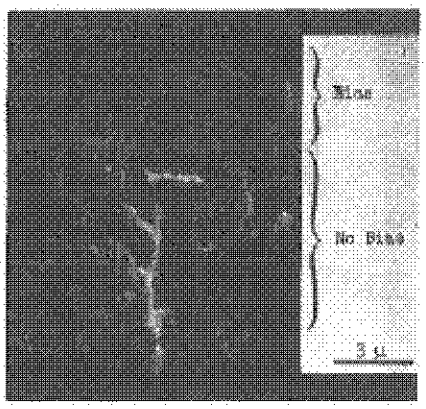

FIGURE 8. Fracture cross section of electron beam evaporated tantalum deposit begun with no bias and then with a bias applied.

Conclusions

It is shown that habit modification and densification of thick deposits can be accomplished by ion bombardment of the deposit during growth. This effect may be attributed to resputtering of the deposit surface during deposition. It should be noted that the deposit bias found most effective in densifying the deposits in this investigation is somewhat higher than normally used in bias sputtering to produce low resistivity, high purity thin films.[20] It is proposed that this general technique of ion bombardment during deposition to densify the deposits can be extended to nonmetals and to other deposition techniques such as chemical vapor deposition.

Acknowledgments

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Attachment 2

Effect of ion bombardment during deposition on thick metal and ceramic deposits*

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Energetic ion bombardment of metal and ceramic deposits during deposition is shown to affect the morphology, structure, stochiometry, and physical properties of the resulting deposit. The bombardment of the growing deposit tends to eliminate the columnar growth morphology normally encountered in thick-crystalline deposits. Generally, in metals it is found that internal stress, density, and gas content increase with increasing ion bombardment energy, but in some cases there is a decrease at high energies, possibly due to heating. In the case of sputter-deposited glass films, it is found that ion bombardment affects the stoichiometry, the coefficient of thermal expansion, and the strain point of the glass. Specific data are presented for thick (> 1 μ) rf sputter-deposited Corning 1720 glass and also sputter-deposited and electron-beam ion-plated chromium deposits with both a dc and a rf substrate bias.

INTRODUCTION

The formation of thick deposits by atomistic deposition processes often leads to a highly columnar morphology with low density. In electrodeposition this columnar morphology may be disrupted by the use of leveling or brightening agents which cause continual renucleation of the growing film by absorbing onto the growing surface.[1] In chemical vapor deposition (CVD)[2] and electrodeposition, the columnar morphology may be disrupted by mechanically disturbing the surface during deposition. In vacuum deposition the columnar morphology may be eliminated, in some cases, by heating the substrate during deposition.[3] It has also been shown that ion bombardment during deposition can alter the growth, density, and appearance of thick-metal deposits produced by CVD,[4] sputter deposition,[5] vacuum evaporation,[6,8] and e-beam ion plating.[6,7] Under some deposition conditions, deposits can exhibit unexpected structural behavior such as the room-temperature recrystallization observed in high-rate sputter-deposited copper.[8] This may be attributed to the high defect concentration and high internal stress present in some deposits. In this paper we discuss the effects of ion bombardment during deposition on the composition, structure, and mechanical properties of thick glass and metal coatings.

MORPHOLOGY

Ion bombardment during deposition can, under proper conditions, eliminate columnar morphology in deposits. Figure 1 shows rf sputter-deposited tungsten films with and without (electrically floating) a dc bias. The films were deposited at the same time. Note the lack of columnar structure in the fracture cross section of the −500-V dc-bias film. In addition, there is a factor of 3 difference in thickness, indicating a much higher density in the −500-V film, since the areal mass of deposited materials is about the same. The same bias effect is noted with rf sputter-deposited chromium films at −500-V bias, i.e., elimination of the columnar morphology as viewed in fracture cross section. On the other hand, dc sputter-deposited tungsten and chromium with a −500-V bias still show a columnar structure in fracture cross section.

Figure 2(a) shows the surface morphology of dc sputter-deposited chromium as a function of bias. Figure 2(b) shows the surface morphology and fracture cross section of rf sputter-deposited chromium with the deposit electrically floating (+50 V) and with a bias of −500-V dc. At zero and positive bias the surface structures are very dendritic. At the higher negative bias the surface becomes very nodular and fine grained. The ion bombardment in dc sputter deposition causes greater changes in the surface texture than in the bulk morphology, as has been noted by other investigators.[4] On increasing the deposit poten-

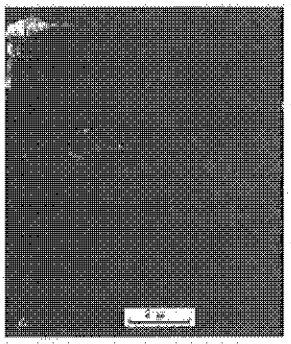

FIG. 1. Fracture cross section of rf sputter-deposited tungsten films on glass with and without (floating) a bias. Both films were deposited at the same time. A—No bias, B—−500-V bias.

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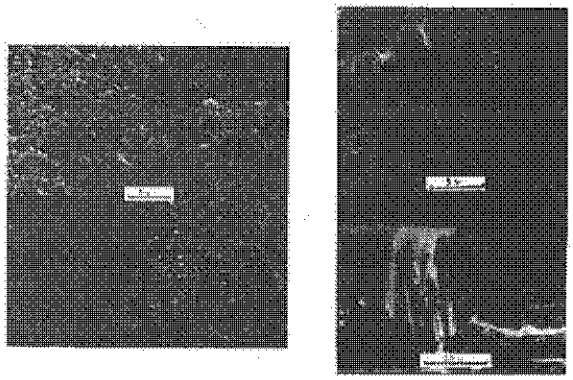

(a) (b)

FIG. 2. Morphology of thick dc and rf sputter-deposited chromium films as a function of substrate bias. (a) Surface morphology of 0, −100, −200, and −500-V dc biased deposits. (b) A—surface (top) and fracture cross section of +50-V (floating) rf sputter-deposited chromium films, B—surface (top) and fracture cross section of −500 volts bias film.

tial from 0 to −500-V dc, the deposition rate of the rf sputter-deposited chromium was found to decrease by a factor of 2, while the rate for dc sputter deposition was found to increase by a factor of 3. Thus the dc sputter-deposited films with a bias had a much higher deposition rate than the rf sputter-deposited films, which could affect the growth morphology.

Chromium films were also deposited by e-beam evaporation (1) in vacuum with no substrate bias, (2) in vacuum with −4-kV dc bias, (3) at 25-μ argon gas pressure with no bias (gas evaporation), (4) in 25-μ argon gas with 2100-V rf bias (gas discharge), and (5) in 25-μ argon with −4-kV dc bias (gas discharge). In no case was the columnar morphology eliminated, although the −4-kV dc bias did tend to decrease the columnar nature of the deposit both in vacuum and in the gas discharge.

With the e-beam techniques the most pronounced change was noticed in the surface morphology. Figure 3 shows the surfaces of the various e-beam deposits. Note that the ion bombardment in the discharge produces a pebbly surface compared to the no-bias condition. It is interesting to note that the application of the −4-kV dc bias to the vacuum-evaporated

FIG. 3. Surface morphology of thick e-beam-deposited chromium films. A—Evaporated at 25-μ gas pressure, B—evaporated at 10^{-5} Torr, C—25-μ, 4-kV dc, D—25-μ, 2100-V rf.

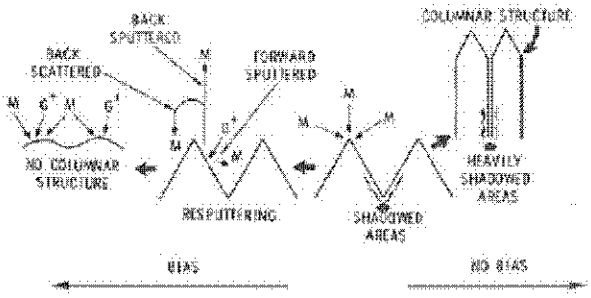

FIG. 4. Model of growth modification by ion bombardment during deposition. Ion bombardment erodes the peaks and fills the valleys by forward sputtering. Some of the backsputtered material is returned to the surface by scattering processes.

chromium increased the deposition rate by a factor of 2 over the no-bias condition even though the deposit current density was only about 0.1 mA/cm². The deposition rate of the e-beam technique was about 25 times greater than that of the sputter-deposited chromium (0.5 vs 20×10^{-3} mg/cm²/min).

In the case of 0-bias rf sputter-deposited glass films deposited on rough surfaces, it was found that a columnar structure is generated because of the substrate surface roughness. With an rf substrate bias (−200 V) the columnar morphology is eliminated.[10]

A model which is proposed for the disruption of the columnar morphology is depicted in Fig. 4. Surface roughness of deposited films is generated either by replication of the substrate surface roughness or by preferential growth of crystallographic planes. Once this roughness develops, geometrical shadowing will prevent deposition in the "valleys" while the "peaks" will grow. This develops the columnar morphology. Ion bombardment, on the other hand, erodes the peaks and "forward sputtering" will fill the valleys. "Backsputtered" material may be returned by scattering processes in the gas, further randomizing the deposition direction. Another effect of ion bombardment is that it creates surface defects which may act as nucleation sites for depositing film atoms.

COMPOSITION

Thick deposits (>5 μ) of Corning 1720 glass were deposited by rf sputter deposition with varying rf

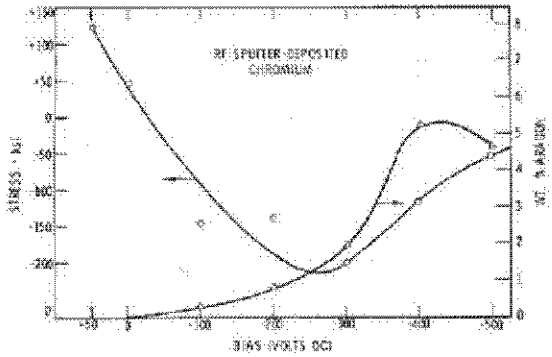

FIG. 5. Stress and gas content of thick rf sputter-deposited chromium films as a function of deposit bias during deposition.

TABLE I. Oxygen depletion before and after annealing of ion-bombarded Corning 1720 glass rf sputter deposited in argon and in argon–5% oxygen gas. Values obtained by neutron activation analysis using bulk glass as a standard.

Gas	Bias	% (±5) depletion	After 600°C in air % (±5) depletion
Ar	+30	3	4
Ar	0	13	13
Ar	−50	17	15
Ar	−100	16	6
Ar	−200	20	8
Ar/O_2	+30	0	0
Ar/O_2	0	6	7
Ar/O_2	−50	13	12
Ar/O_2	−200	18	15

biases (+30 to −200 V) on the deposit.[10] This glass, whose coefficient of thermal expansion (CTE) closely matches that of tungsten, contains a number of minor constituents, the concentrations of which were unaffected by ion bombardment. The Si/O ratio, as determined by neutron activation analysis, was found to be very dependent on substrate bias, as is shown in Table I. The Si/O ratio is shown as a function of bias during deposition, sputtering gas (pure argon or argon–5% oxygen) both as-deposited and after a 600°C, 1-h heat treatment in air. Note that sputtering in the argon–oxygen mixture does reduce oxygen depletion in low bias films (+30, 0, −50 V) but does not appreciably change the depletion at high negative biases (−200 V). In fact, after air annealing, the high bias films sputtered in pure argon show less oxygen depletion than annealed films deposited in the argon–oxygen mixture.

No such compositional studies have been made on metal alloys, although it has been shown that there are compositional changes in sputter-deposited stainless steel when there is no intentional ion bombardment.[11]

STRESS

In all of the metal systems that we have investigated, the film compressive stress increases with negative bias. In most systems the stress seems to reach a maximum value at −200 to −300-V dc bias then decrease. Figure 5 shows the stress in rf sputter-deposited chromium films as a function of substrate bias.

A compressive stress which increased with bias was also seen in rf sputter-deposited Corning 1720 glass. In addition, the glass films deposited in argon at low substrate bias (+30, 0, −50 V) show an erratic behavior in the coefficient of thermal expansion on initial heating.[10] Figure 6 shows the behavior of one such film deposited on a tungsten beam on initial heating and after annealing at 600°C. After annealing, the films are well behaved and have a CTE approximately that of bulk 1720 glass even though there is appreciable oxygen deficiency in some films. Films deposited at high bias (−200 V) show no erratic behavior on initial heating. The erratic behavior would indicate

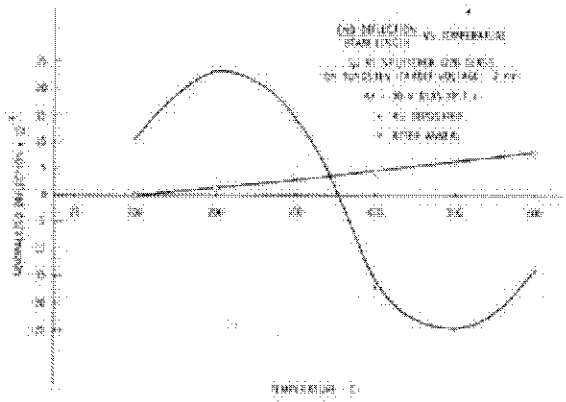

FIG. 6. Thermal expansion behavior of Corning 1720 glass films rf sputter deposited on a tungsten beam in the as-deposited and annealed case (extreme example).

annealing at temperatures far below the strain point of the bulk glass (670°C). This may be attributed to high internal stress and a metastable structure in the as-deposited film.

DENSITY

In all cases which we have studied, ion bombardment increases the density of the deposit over that of the no-bias case. Figure 7 shows the density of thick chromium films both sputter deposited (rf and dc) and e-beam evaporated (vacuum and in a gas discharge). Only in the case of rf sputter-deposited films does the density reach a maximum then decrease with increasing bias. It is interesting to note in the case of rf sputter-deposited chromium that the density does not relate directly to the observed morphology. At maximum density (−100-V) the columnar structure is still quite apparent. At −500-V bias the columnar structure has entirely disappeared but the density has decreased from its maximum value. The only measured property which seemed to correlate with rf sputter-deposited film density was the degree of preferred crystallographic orientation. The sample with the

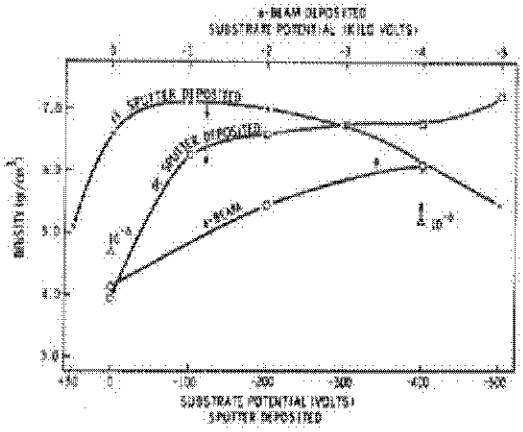

FIG. 7. Density of thick chromium deposits formed by dc and rf sputter deposition, e-beam evaporation at 25-μ gas pressure (gas discharge when voltage applied), and at 10^{-6}-Torr vacuum.

greatest density (−100-V dc bias) had the most random crystallographic orientation. Note that even at the high deposition rates associated with e-beam deposition, the bias and associated ion bombardment cause appreciable increases in deposit density.

GAS CONTENT

Gas content is also affected by bias. Figure 5 shows the argon content of rf sputter-deposited chromium. Ion bombardment during deposition can be used to deliberately incorporate large quantities of sputtering gas in the deposited material.[12] At high biases there is a decrease in gas content, probably due to heating. Gas incorporation can be minimized by heating the deposit during deposition.

SUMMARY

Ion bombardment may be used to modify the morphology of deposited coatings. The reason for the greater effect of ion bombardment on rf sputter-deposited material compared to dc sputter-deposited material is unknown. There is apparently a minimum ion/depositing-atom ratio needed to be effective in disruption of the columnar morphology. Ion bombardment during deposition can also increase the deposit density, particularly when compared to sputter deposition onto electrically floating-insulating substrates. Ion bombardment may also alter the composition of alloy and compound systems. The intrinsic stress and gas content of the deposited material also depend on the ion bombardment, and these properties may be important to the physical properties of the deposited material.

ACKNOWLEDGMENTS

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Attachment 3

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Physical Properties of Thick Sputter-Deposited Glass Films

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ABSTRACT

The coefficient of thermal expansion (CTE) of 5μ thick rf sputter-deposited Corning 1720 glass films was measured using a cantilever beam technique. The films were rf-bias sputtered in an argon (Ar films) and an argon-5% oxygen (Ar/O_2 films) gas mixture. The Ar films deposited with a low substrate bias (+30, 0, and −50V) exhibited an erratic CTE on initial heating but were well behaved after a 600°C air anneal. High bias (−100, −200V) Ar films and Ar/O_2 films showed no erratic behavior on initial heating. Chemical analysis indicated no significant change in the minor constituents of the sputtered glass, but neutron activation analysis showed a progressively greater oxygen depletion with increasing negative bias for both the Ar and Ar/O_2 films. Etch rates were shown to increase with increasing negative bias. It is suggested that the structural changes that occur in some glass films at temperatures far below the strain point of the bulk glass (670°C) are due to a combination of intrinsic stress and a high concentration of defects. Surface coverage by the sputter-deposited glass films is discussed.

The use of sputtered films of any type has several potential problem areas: (*i*) The films may contain high concentrations of defects and be highly stressed. This may be reflected in unusual physical behavior such as the room temperature structural changes noted in high-rate sputter-deposited copper (1). (*ii*) For complex materials such as glasses, alloys, and compounds, there may be compositional changes during deposition (2) which can affect the properties of the material. For SiO_2, oxygen depletion is a commonly observed compositional change (3). (*iii*) Sometimes there are unusual structural and crystalline modifications found in sputter-deposited films which may give properties differing from those of the bulk material (4). It is the exception rather than the rule when deposited films have bulk properties.

Generally, the physical properties of thin sputter-deposited glass films are not of great concern; however, as the film thickness increases, the properties may become important in specific applications. In this investigation, the coefficient of thermal expansion (CTE) of 5μ thick rf sputter-deposited glass films was investigated as a function of substrate bias during deposition and as a function of sputtering gas composition. It was found that after annealing, the sputter-deposited films had a CTE close to that of the bulk glass. Before annealing, films deposited under some conditions showed an erratic behavior of the CTE.

The ability of the deposited films to cover surface topography was also studied. Generally, it has been found that films deposited by some type of negative substrate bias deposition technique show a better ability to cover surface discontinuities than do films deposited with no bias (5).

Key words: sputtered glass films, bias, strain point, surface coverage, composition, coefficient of thermal expansion.

Experimental

An axially symmetric sputtering system with a planar diode design was used to rf sputter deposit the glass films (6). The substrates were clamped to an electrically isolated, water-cooled holder which was an integral part of the top plate of the vacuum system. This "sputter-up" design was used to minimize the problem of dust and debris falling on the substrate and causing pinholes. The 0.6 cm thick Corning 1720

glass (an alumino-silicate glass) plate used as a sputtering target was laid on a water-cooled copper block. A problem was encountered in nonuniform heating of the glass plate during sputtering, causing cracking. The edges of the cracks then showed increased sputtering rates. Copper was also found to migrate along nonseparated cracks, giving contamination in the deposited film. This problem was alleviated by the insertion of a 0.3 cm thick fused quartz plate between the 1720 glass sputtering target and the copper cooling block.

The rf sputtering supply was a commercial MRC Model 3007 unit capacitively coupled to the target and substrate holder by conventional "L" tuning networks. Power input and rf peak voltage were held constant during deposition and the reflected power was minimized. Substrate biases were obtained either by tuning the substrate with respect to ground (7) to obtain low positive (+30V), zero, and low negative (−50V) biases, or by utilizing the rf splitting network on the power supply to obtain higher negative biases (−100 and −200V).

A shutter which could be rotated in a plane parallel to the electrodes and moved vertically was used in the system. This shutter allowed sputter cleaning of the substrates and presputtering of the target without cross contamination. It also allowed slow target warm-up and a stable sputtering condition to be established before beginning sputter deposition on the substrates.

A target-substrate distance of 7 cm was used throughout the investigation. A 50 oersted axial magnetic field was used for all depositions except for the high negative bias conditions where the magnetic field prevented the establishing of a stable discharge.

Commercial pure argon (Ar) gas and an argon-5% oxygen (Ar/O_2) gas mixture was used for sputtering. Flow rates were controlled using a variable leak while the gas pressure was monitored using a Schultz-Phelps high pressure ionization gauge. Vacuum system throughput was controlled by throttling the gate valve. The gas inlet was in the top of the chamber, and gas was removed through the baseplate.

For measurement of physical properties, glass films deposited in pure argon (Ar films) were deposited on 1 × 7 cm tungsten beams 0.1 mm thick. When using Ar/O_2, plasma oxidation of the tungsten was excessive and the glass films (Ar/O_2 films) were deposited on 0.2 mm thick alumina beams. Films for chemical analysis were deposited on carbon, high resistivity low oxygen silicon slices, and low gas content platinum. The substrates were clamped to the water-cooled substrate block using no contacting material.

In order to cover steps and defects, film thicknesses of 5-10μ were desired. With the sputtering conditions used, the deposition rate was about 1 μ/hr (4 $\mu g/cm^2/min$). The sputtering rate in Ar varied from 5 $\mu g/cm^2/min$ at 2 kV target potential and +30V bias to 3 $\mu g/cm^2/min$ at −200V bias. Rates in Ar/O_2 showed the same variation with bias and about a 20% decrease in deposition rate at a given bias as compared to argon sputtering. This decrease of sputtering rate with the addition of oxygen is appreciably less than that reported in the literature for sputtering SiO_2 films (8).

The substrates were solvent cleaned before being mounted in the vacuum system. The vacuum system was pumped to 5×10^{-6} Torr, after which the gas inlet was opened and gas flow regulated to give 1μ indicated pressure in the chamber. The gate valve of the vacuum system was then throttled to give a final pressure of 10μ in the chamber. The pressure was monitored throughout the deposition.

The substrates were sputter cleaned at 1 kV rf for about 30 min with the shutter covering the sputtering target. The shutter was then moved to cover the substrates and the target was presputtered. The presputtering of the target was done by slowly increasing the input power so as to allow gradual heating of the target to prevent shattering from thermal shock. The target voltage was raised to 2 kV peak-to-peak rf which required a power level of about 1000W to the 15 cm diameter target.

After steady state was established, the shutter was opened and the deposition was made for a predetermined time to give the desired film thickness. After the deposition was complete, the system was allowed to cool under vacuum before the films were removed. In order to form pinhole-free films, it was found necessary to deposit the film using two to three depositions. Between depositions the substrates were removed and the surface rubbed with acetone on a lint-free cloth. This procedure apparently moved or removed particulate contamination to the extent necessary to prevent pinholes from propagating through the several glass layers. The layers were lightly sputter cleaned between depositions.

After deposition the coated beam was mounted in a muffle furnace having an optical window in such a way that the deflection on heating was perpendicular to the gravitational field to eliminate gravitational deflection. The cantilevered beam was then heated in 100°C increments and the deflection of the free end was measured using an optical cathetometer.

The radius of curvature ρ of the beam was then determined using the equation

$$\frac{1}{\rho} \approx \frac{2\delta}{L^2}$$

where δ = the deflection of the end of the beam and L = the beam length.

The coefficient of thermal expansion (CTE) was calculated using the equation (9, 10)

$$\frac{1}{\rho} = 6(\alpha_f - \alpha_s)\Delta T(1+m)^2/h \left\{3(1+m)^2 + (1+mn)\left(m^2 + \frac{1}{mn}\right)\right\}$$

where ρ = radius of curvature, α_f = expansion coefficient of film, α_s = expansion coefficient of substrate, ΔT = temperature increment, m = thickness of substrate/thickness of film, and h = total thickness. Bulk modulus values were used for the glass film.

Results

Figure 1 shows the normalized beam deflection of an Ar +30 film (argon gas, +30V bias) as a function of temperature. On initial heating, the deflection is seen to vary erratically and actually change sign. Other Ar low bias films showed the same behavior on initial heating, though not as radically as did the Ar +30 films. The Ar/O_2 films did not show this erratic behavior with the exception of the Ar/O_2 −50 films, in

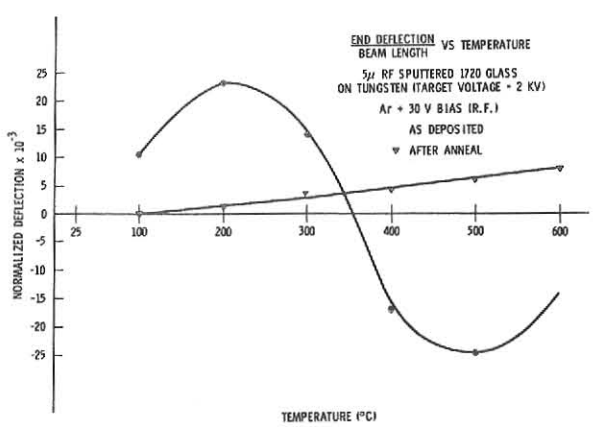

Fig. 1. Deflection of beam end showing typical behavior of an as-deposited film and an annealed film (extreme examples).

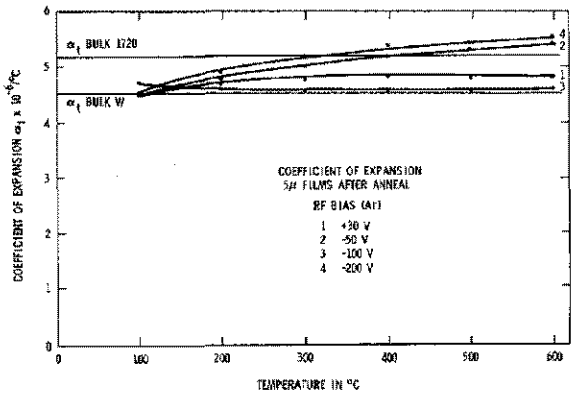

Fig. 2. Coefficient of thermal expansion of 5μ thick glass films after annealing as a function of rf bias on the substrate during deposition. Values accurate to ± 10%.

which it occurred to a slight extent. Initial deflection of the beam at room temperature showed that the Ar +30 as-deposited films had a high compressive stress.

After annealing to 600°C in air for less than 1 hr, all beams showed the type of deflection shown by the straight line in Fig. 1. Figure 2 shows the CTE of Ar films prepared with various biases after annealing compared with the literature values of bulk tungsten and bulk Corning 1720 glass in the 0°-600°C temperature range. The values compare very well. The CTE of the Ar/O_2 films was very close to that of the annealed Ar films. The initial erratic behavior of the Ar films was the source of some concern since stress during initial heating might cause failure in service.

The deposited glass films were analyzed by emission spectroscopy for the minor constituents which normally control the CTE. There was no appreciable change in the minor constituents of the sputter-deposited Ar glass films compared with those of the bulk glass. Neutron activation analysis of the silicon-oxygen ratio was made on the glass films using bulk 1720 glass as a standard. Table I shows that the oxygen depletion is greatest in the high negative bias Ar and Ar/O_2 films. Low bias Ar/O_2 films and the Ar +30 films show the least oxygen depletion. Some oxygen was recovered on annealing the high bias Ar films in air at 600°C, but little oxygen change was noted in the Ar/O_2 films on annealing. The oxygen depletion was also evident in the color; near stoichiometric films were clear and nearly colorless while the oxygen-deficient films had a brown coloration.

The *IR* transmission of thin films (5000Å) deposited on high purity, low oxygen silicon was studied. The +30V films show a broad absorption peak in the range 1100-900 cm^{-1}. The −200V films show a definite Si-O stretching band at about 1100 cm^{-1}. In the Ar +30V film a definite shift of 25 cm^{-1} toward shorter wavelengths was found on annealing, suggesting a bond length change due to stress relief (11, 12) or change in composition. The low bias Ar films also showed appreciable moisture pickup at room temperature, as evidenced by the absorption peak at 3333 cm^{-1} in the as-deposited films. The high bias Ar and Ar/O_2 films showed no such water pickup.

Table I. Oxygen content of glass films as a function of deposition conditions and subsequent anneal. Values obtained by neutron activation analysis using bulk glass as a standard

As deposited Gas	Bias	% (±5) depletion	After 600°C in air % (±5) depletion
Ar	+30	3	4
Ar	0	12	13
Ar	−50	17	15
Ar	−100	18	8
Ar	−200	20	8
Ar/O_2	+30	0	0
Ar/O_2	0	6	7
Ar/O_2	−50	13	12
Ar/O_2	−200	18	15

Thick films (~100μ) were deposited for etch rate studies. A region was masked using acid stopoff and the films were etched in "P-etch" (13)[1] for a period of time sufficient to give about a 25μ step in the glass. After etching, the acid stopoff was removed and the step height was measured using a Talysurf profilometer. Figure 3 shows the etch rates for Ar and Ar/O_2 as-deposited films. The etch rates increased with negative bias and even in the best films, exceed the rate of bulk 1720 by a factor of 2. The high bias films showed bubbling on etching while the low bias films showed no bubbling. After annealing to 600°C in air, the films became fragile, the etch rates approached that of the bulk, and no bubbling was observed on etching. Fusion analysis shows several weight per cent (w/o) argon in the −200V Ar and Ar/O_2 films before annealing and zero (0.01 w/o detection limit) to several tenths of a weight per cent in the zero bias films.

The ability of the sputter-deposited glass films to cover surface discontinuities was found to be very dependent on the type of discontinuity. As shown in Fig. 4, a 5μ glass film covered a 5μ step very well but did not bridge over a void in the surface. Very thick films can fill a void to some extent, as shown in Fig. 5, but the geometrical shadowing of void walls tend to leave a "pipe" of unfilled void. If the void geometry is such that the bottom and walls are out of the line of sight from the target, such as shown in Fig. 6, incomplete sealing of the void can result. This is also the case if the depth of the defect is large compared to the width.

It was found that a high negative rf bias on the substrates during deposition caused appreciable changes in the film morphology when the films were deposited on a surface having severe topological features. Figure 7 shows a fracture cross section of thick glass films deposited on a grainy carbon surface with a +30 and −200V bias. The low bias films show a columnar structure similar to that observed in thick metal films (4). The bias-deposited films show no such structure. The columnar structure is attributed to geometrical shadowing effects as the film is deposited over the rough surface. Ion bombardment of the bias-deposited film during deposition causes resputtering which tends to erode peaks and fill valleys, thus preventing the development of the columnar structure (4).

[1] P-etch = 15 parts hydrofluoric acid, 10 parts nitric acid, and 300 parts water.

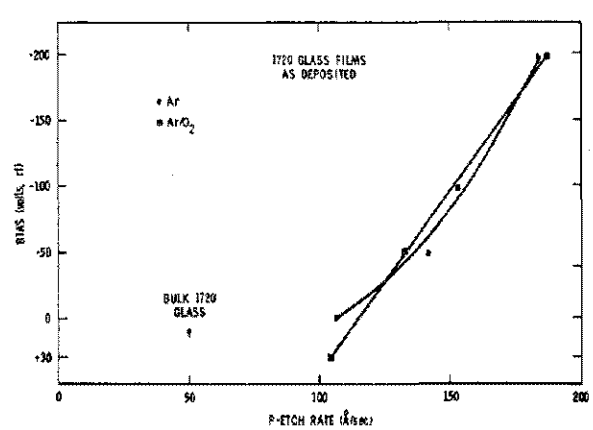

Fig. 3. Chemical etch rate of as-deposited films as a function of bias during deposition (P-etch is 15 parts HF, 10 parts HNO_3, and 300 parts H_2O).

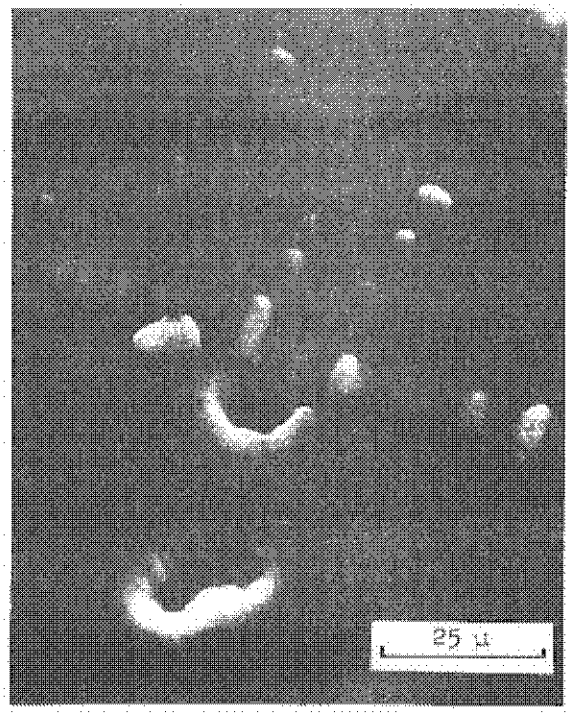

Fig. 4. A 5μ thick tungsten step on a porous surface coated with 5μ of glass. Note that the glass layers did not bridge over the pore in the substrate [scanning electron microscope (SEM)].

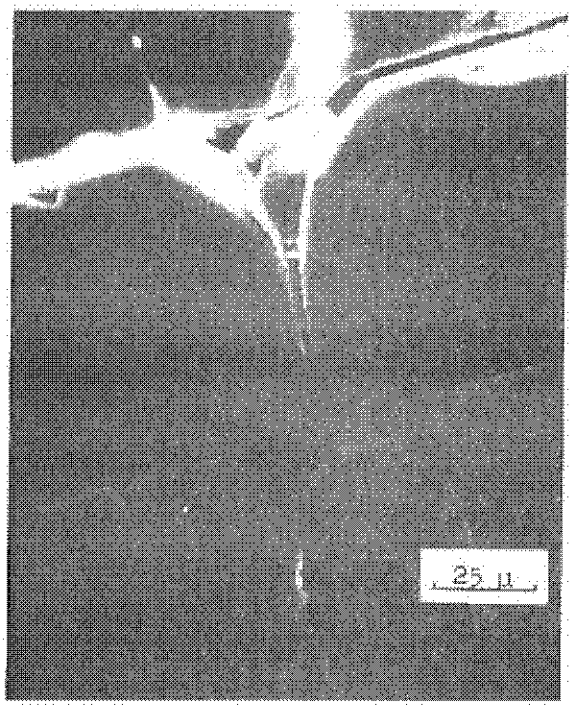

Fig. 5. Very thick glass film deposited over large defect between glass bonded plates. Note the "pipe" of unfilled void caused by geometrical shadowing (SEM fracture cross section).

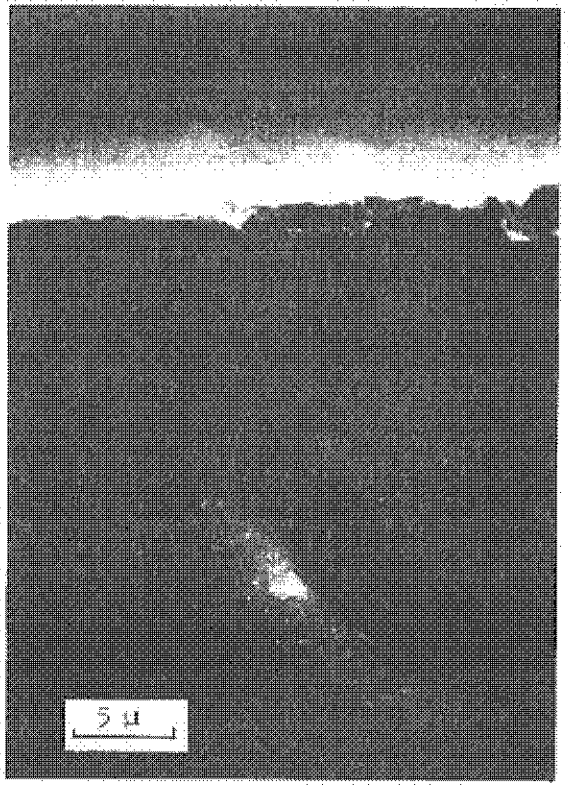

Fig. 6. Small pore in which the bottom is uncoated because of the inability of the depositing glass to reach the bottom either by migration or resputtering (−50V bias) (SEM fracture cross section).

Discussion and Conclusions

These data indicate that the sputter-deposited 1720 glass films may show structural changes, as evidenced by the CTE behavior, at temperatures as low as 300°C, which is far below the strain point of the bulk glass (670°C). The effect is particularly pronounced in films sputtered in pure argon with a low bias on the substrate during deposition. The effect is less pronounced with high substrate biases, probably due to heating during deposition. The effect is also less pronounced when the films are sputter deposited using an Ar-5% O_2 gas mixture for the sputtering gas. After annealing, all films showed a well-behaved CTE and have values close to that of the bulk glass.

All films deposited using pure argon as the sputtering gas showed oxygen depletion. The oxygen depletion increases with negative bias for both Ar and Ar/O_2 films. The oxygen depletion did not seem to drastically affect the CTE of annealed films.

Optical analysis data are not definitive because of the lack of sharply defined adsorption peaks. These data indicate some shift in the Si-O absorption peak in the low bias Ar films with annealing due either to stress relief or compositional change.

The etch rate data seem to be inconsistent with the other data if compared to similar data for SiO_2 films (13). In deposited SiO_2 films, oxygen depletion leads to decreased etch rate while stress and radiation damage give an increased etch rate. In this study the increased etch rate with the substrate bias may be due to appreciable argon incorporated in the deposited films at the high negative biases (14, 15) as well as the ion bombardment damage introduced during the deposition.

It seems that the most stable stoichiometric films are produced by sputtering in Ar/O_2 with a zero or slightly positive (+30V) bias. Films having stable CTE's can be deposited by applying a negative rf substrate bias during deposition, though this leads to an oxygen deficiency. The bombardment during deposition probably causes heating, which anneals the film. A similar effect could probably be obtained by

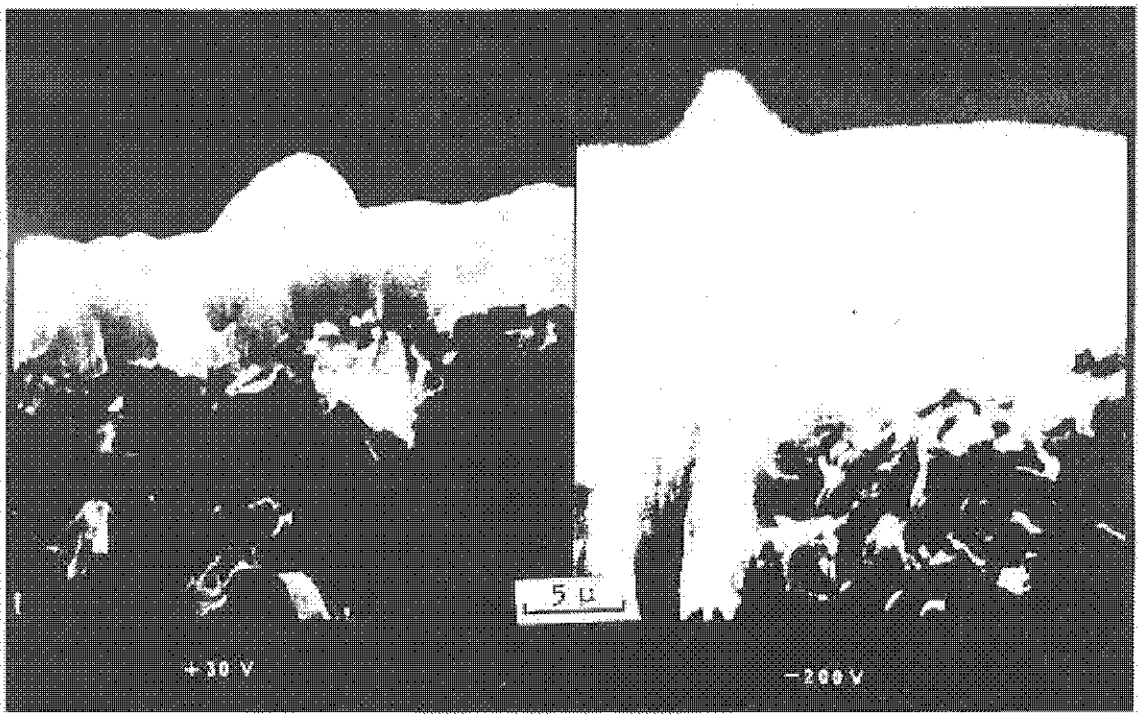

Fig. 7. Fracture cross section of glass films deposited on grainy carbon surfaces with and without a negative substrate bias during deposition. Note the isotropic morphology of the deposit made with a negative substrate bias (SEM).

heating the films to 300°-400°C during deposition. The ion bombardment during deposition could have the undesirable effect of incorporating appreciable amounts of inert gas into the film which could be released during subsequent heating.

The origin of the initial erratic CTE behavior of some films does not appear to be directly related to oxygen deficiency since the most erratic films (+30 Ar) show little oxygen deficiency. It is suggested that a combination of high intrinsic film stress and a high concentration of point defects is the origin of the initial behavior of the CTE. This is consistent with the findings for neutron and x-ray irradiated glasses where low temperature annealing of such defects is noted in their optical behavior (18).

Though the bias deposition of the glass films did significantly change the structure of the films and improve the defect-covering ability, it was still unable to cause complete coating of some defects.

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Attachment 4

DEPOSITION OF CdS BY EVAPORATION THROUGH A GAS DISCHARGE*

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ABSTRACT

Cadmium sulfide is an important material used in thin-film photovoltaic devices. The deposition of cadmium sulfide films by single indirect source evaporation through a gas discharge is investigated and the effects of the discharge on film properties and deposition rates are discussed. The discharge has a direct and advantageous effect on both the electrical and optical properties of the CdS thin films. These properties may be controlled by suitable choices of evaporation and gas discharge parameters. Control of these properties is important in device applications and it is proposed that this technique is a practical method for controlling properties of CdS thin films such as doping and morphology.

*Supported by the U. S. Atomic Energy Commission.

INTRODUCTION

Cadmium sulfide has been used as a semiconductor in thin film photovoltaic cells for many years.[1] This semiconductor material is generally deposited by direct thermal evaporation in a vacuum at rates sufficiently low to assure that, after further processing, the resistivity will be of the required value (about 10 to 100 Ω-cm).[2,3] Resistivities obtained in this way have been attributed to a slight deficiency of sulfur in the deposit.[4] Although there have been studies on several aspects of these films,[5,6,7,8] such films, particularly those used in solar cell devices, remain largely uncharacterized due to their complexity.

There have been several notable studies on the behavior of cells fabricated with pure, single crystal material.[9,10] In these experiments, single crystals of CdS with high intrinsic resistivity were doped to the desired resistivity. High purity, high resistivity polycrystalline CdS samples also have been made in thin film form, generally for photoconductor, acoustoelectric, or other non-photovoltaic devices. Such films have been deposited by vacuum evaporation either by using a relatively complex two-source technique[11,12] or by restricting the deposition rate to very low values[3] ($\lesssim$ 1Å/sec) in order to maintain stoichiometry. The films are characterized by a relatively high resistivity and by an oriented, hexagonal polycrystalline structure.[3,7]

Similar properties have been reported for sputtered CdS films,[13] but they have also been deposited at relatively low rates. The sputtering process has been studied in great detail, and some of the factors

influencing the stoichiometry and structure have been identified. Limiting the vacuum system throughput, for example, can limit the flushing of sulfur from the system, which is an effect that is similar in some ways to growth of crystals in a sealed ampule.[4] There have been reports that the carrier type as well as concentration can be controlled in several II-VI compounds by doping during deposition.[14,15] Ion bombardment during sputter deposition of other materials can result in re-emission of components which are in excess of that required for stoichiometry.[16]

In this investigation, we have attempted to devise a simple technique for high rate deposition of CdS by evaporation which will yield films with high intrinsic resistivity and which can be easily doped during deposition. The technique consists of single source evaporation through a gas discharge containing volatile compounds of the constituents desired in the film. This general technique with no substrate bias has been termed activated reactive evaporation.[17] Using a discharge with a substrate bias, the deposition has been termed chemical ion plating.[18] This paper discusses the quality of films obtained by this technique and discusses the effects of some of the deposition variables. It is suggested that this technique can be extended to the growth of films with controlled doping levels.

EXPERIMENTAL TECHNIQUE

Thin film samples of CdS were produced in a standard oil diffusion pumped vacuum system which had an ultimate vacuum in the low 10^{-7} Torr range. The source material was 5N pure pressed CdS pellets*

*MRC MARZ grade power pressed into pellets.

sublimed from a Mathis "baffled box" source.* Substrates were standard microscope slides mounted on a water cooled substrate table about five inches above the source (Fig. 1). The table could be electrically biased. A shutter shielded the substrate until the source was stabilized. A discharge ring electrode which was concentric with the rest of the system was placed between the substrate and source. For depositions utilizing a discharge, either argon or an argon-0.85% hydrogen sulfide mixture was admitted to the system to 5×10^{-4} Torr pressure. The high-vacuum valve was then throttled to give a system pressure of 10^{-2} Torr. The 10^{-2} Torr pressure was selected since it was the lowest pressure at which the discharge was stable and would maintain itself at relatively low voltages without additional electrodes. It was desirable to have low pressure in order to permit high deposition rates and low voltage to minimize sample damage due to bombardment by high energy particles from the plasma. Just prior to opening the shutter, a high negative voltage (generally -2kV) was applied to the ring. Subsequent to deposition, the system was allowed to cool and the films were removed.

Depositions were made at various source power levels with a) no gas in the system (normal vacuum evaporation), b) Ar discharge in the system, and c) Ar-0.85% H_2S discharge in the system in order to identify general characteristics of the system and effects of the discharge on film properties.

Electrical resistivities of the films were measured at room temperature using a dc van der Pauw method.[19,20] Samples were 1 inch squares with contacts at the corners. Initially indium-gallium contacts[21]

*R D Mathis Co. model SM-10

Electrical resistivities were measured at room temperature using a dc van der Pauw method.[19,20] Samples were 1 inch squares with contacts at the corners. Initially indium-gallium contacts[21] were applied to the films immediately after removal from the vacuum system. However, variable and high contact resistances were found on the higher resistivity films. Improved contacts were made by sputter cleaning in argon and vacuum depositing indium. Some lower resistivity samples (1-100 Ω-cm) were measured using an in-line four point probe method with pressure contacts. Dark resistivity values were measured after samples had equilibrated from 80-100 hours in the dark. Light resistivities were measured under an intensity of 45 mW/cm^2 from a Xenon lamp after stabilization for approximately 20 minutes.

It was found that on the high resistivity samples deposited in a discharge, a more conductive material was deposited on the side of the glass slide, which was a low re-emission surface.[16] This layer had to be removed before reliable measurements could be made.

A Beckman DK-2 spectrophotometer was used for optical transmission studies.

EXPERIMENTAL RESULTS AND DISCUSSION

The initial series of samples was made by thermal evaporation in vacuum. This series indicated that there was a very narrow range of source temperatures over which relatively good samples could be obtained. A typical good sample had a resistivity between 1 and 10 Ω-cm, exhibited a relatively sharp optical absorption edge at approximately the energy

of the band gap (2.4 eV) and appeared yellow-green. At slightly higher source temperatures, samples had resistivities less than 1 Ω-cm, were generally metallic in appearance with very little optical transparency, and had a very soft optical absorption edge well below the energy of the band gap. Higher source temperatures generally produce a difference in evaporation rates between the cadmium and sulfur which cause the evaporant to become cadmium enriched.[22] This together with water cooling of the substrate probably produced a softening of the optical cut-off and a decrease of the cut-off to lower energies. None of these samples showed any photoconductivity.

With the argon discharge sample resistivities could be increased, and the absorption edge became somewhat sharper than those for vacuum evaporated films at the same source temperatures. In addition, the range of source temperatures for which resistivities were greater than 1 Ω-cm was extended. Samples with resistivities of 10-100 Ω-cm showed very slight photosensitivity, with only 20 to 30% increases in resistivities from light to dark conditions.

When the Ar-0.85% H_2S mixture with a -2kV discharge potential was used, some of the dark resistivities of as-deposited samples increased to more than 10^7 Ω-cm. The films became quite photosensitive and the optical cut-off became much sharper at the band gap energy. Although it is generally agreed that heating of the substrate increases the resistivity for both vacuum evaporated and sputtered films,[3,13] no experiments have yet been performed using heated substrates due to the limitations of our apparatus.

Most of the samples in this series were deposited using a -2kV discharge potential on the ring electrode and were deposited thicknesses of 1-1.5 μm at rates of about 500Å/min. The sample thicknesses were chosen to be above the range reported to produce appreciable modification of the resistivity due to surface scattering,[5] and at the same time were thin enough to prevent any serious depletion of source material from the relatively small source. Good samples were generally in the range of 10^6-10^7 Ω-cm. These samples exhibited moderately strong photo-responses, with dark/light resistivity ratios of about 1000.

The deposition process showed good short term stability and reproducibility. Sets of samples made with progressively more negative biases (0-400v) tended to increase in resistivity by almost a factor of 10. This increase is probably a result of increased sample bombardment by particles from the discharge, which caused heating and resputtering of the film components.[16] Morphology changes may also have occurred such as those observed on both metals and insulators.[2,3]

The effect of the discharge was observed quite dramatically on a set of samples made by changing the discharge voltage. Dark resistivities increased by 2 orders of magnitude from about 10^6 to > 10^8 Ω-cm when the discharge voltage was increased from 2.0kV to 2.5kV. The corresponding increase in substrate current was from 1 mA to 1.5 mA, implying an increase in the strength of the ion bombardment.

CONCLUSIONS

It has been shown that resistivities of CdS greater than 10^7 Ω-cm can be obtained by thermal evaporation in a gas discharge containing H_2S at deposition rates of about 500 Å/min. It is felt that this technique can be further optimized to give samples with higher resistivities and at higher deposition rates than have been observed so far. The deposition technique may also yield better control of properties during device fabrication and can be extended to controlled doping of the CdS during deposition. It is suggested that this technique is a practical method for controlling properties of CdS.

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FIGURE CAPTIONS

Fig. 1. Arrangement of components for deposition of CdS through a gas discharge.

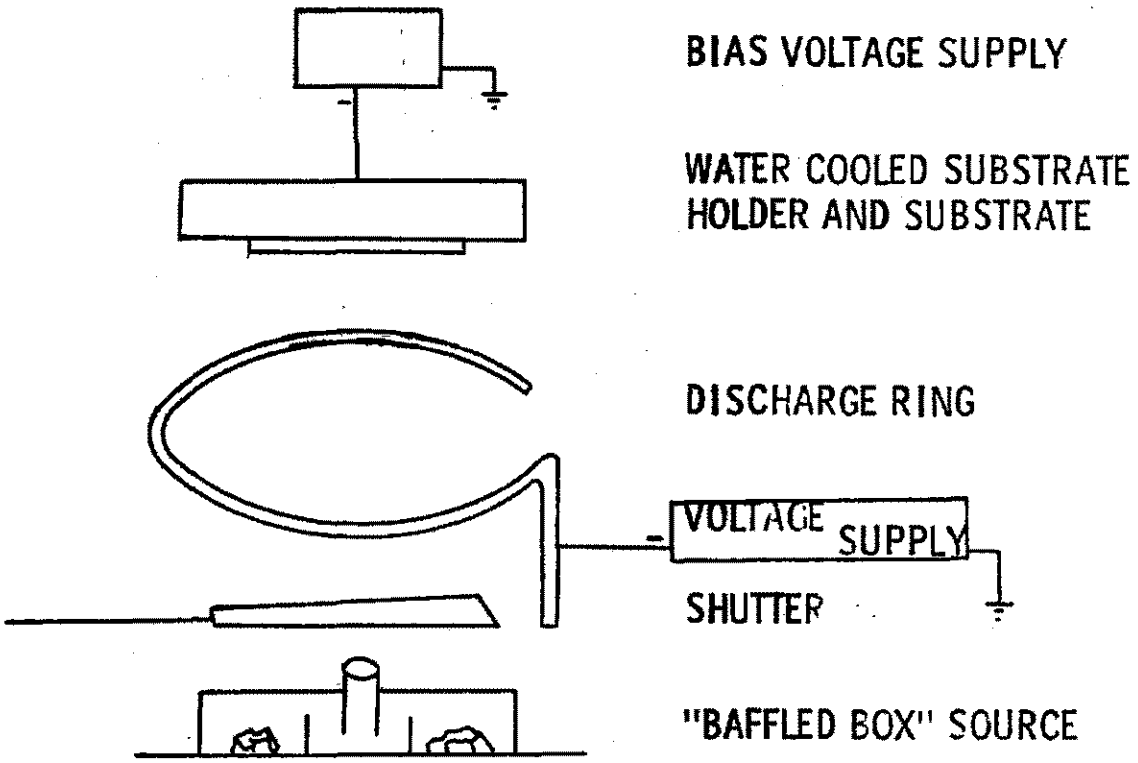

Fig. 1. Arrangement of components for deposition of CdS through a gas discharge

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