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COATING SCIENCE AND TECHNOLOGY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An ion plating unit was constructed and some preliminary studies made using germanium and cadmium telluride as the principal materials deposited. Both glass and potassium chloride were utilized as substrates.

Electron microscopy was used to characterize some organic films produced by plasma polymerization. Electron micrographs, selected area diffraction, and high resolution diffraction techniques were utilized. The crystalline films gave reflections which indicated a cubic system which could be indexed as diamond. Work continues on the automation and computer control of the

ellipsometer and the ion scattering spectrometer.

COATING SCIENCE AND TECHNOLOGY

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TECHNICAL SUMMARY

Technical Problem and Methodology

The objective of this research program is to develop a thorough understanding of the science and technology of films applied as coatings on materials transparent to 10.6 and 3-5 micrometer radiation. The approach includes preparation of films by sputtering, ion plating and plasma polymerization techniques. The materials utilized for deposition were mainly cadmium telluride and the substrates were potassium chloride. Tetrahedral carbon films and organic films formed by plasma polymerization have also been investigated. Techniques for characterizing the films include IR spectroscopy, laser Raman spectroscopy, SEM, electron microprobe, ion scattering spectrometry, Auger electron spectrometry, and ellipsometry.

Technical Results

An ion plating unit was constructed and utilized to prepare films of germanium and cadmium telluride. Both glass and potassium chloride substrates were used. Because of the nature of the ion plating process, the films were coherent and extremely adherent to the substrates. Further characterization is necessary to compare the properties of these films with those prepared by rf sputtering.

Films prepared by plasma polymerization were characterized by electron microscopy using electron micrographs for texture comparison, selected area diffraction for phase identification, and high resolution diffraction to check the selected area diffraction results. Some of the films were amorphous and some were small crystallites in an amorphous second phase. The closest pattern fit was a cubic system with the lines indexing as "diamond". No (00ℓ) graphite lines were obtained. Three graphite (00ℓ) lines were obtained from one area of one film by glancing angle diffraction, pointing out the need for more extensive study. The presence of a "diamond-like" diffraction pattern does give support to a previously hypothesized tetrahedral carbon building-block structure for these films.

Work continued on the preparation and characterization of cadmium telluride films on potassium chloride substrates. Ion scattering and Auger electron spectrometric compositional profiles showed that oxygen does not diffuse into the film. However, an artifact of the Auger electron spectrometric measurements was the enhanced diffusion of chlorine through the film to the surface.

The oxidation of germanium was studied by ion scattering spectrometry. Previous oxidation studies were conducted on low density amorphous films. The current studies were done on high density films. Although oxygen was found throughout the film to the interface, bulk oxidation did not occur in the time period of the studies.

DoD Implications

The results of these studies will be used to provide guidelines for the selection of the best materials, processes and process controls for the production of good optical coatings for infrared components at wavelengths of 10.6 and 3-5 micrometers. The plasma polymerization technique may lead to a new process for the deposition of "diamond-like" films for sealing and protecting optical components.

Further Research

Since funds have been withdrawn leaving the contract with only enough to operate until 31 August 1975, the remaining work will be directed toward completing those studies already in progress. No research will be done on ternary films.

Specific Comments

No specific comments are offered at this time.

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COATING SCIENCE AND TECHNOLOGY

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1. INTRODUCTION

The objective of this research program is to develop a thorough understanding of the science and technology of films applied as coatings on materials transparent to 10.6 and 3-5 μm radiation. The approach includes the preparation of films by sputtering or ion-plating, chemical and physical vapor deposition, and plasma polymerization. The materials to be studied primarily are inorganic, elemental and compound. An extension here will be the exploration of the possibility of sputtering of ternary compounds effectively. New efforts to deposit tetrahedral carbon films are also included. Characterization techniques for the coatings include infrared spectrometry, laser Raman spectrometry, ion scattering spectrometry, Auger electron spectrometry, scanning electron microscopy, x-ray diffraction, x-ray emission analysis, ellipsometry, and durability tests. Both single and multilayer films are to be evaluated on selected substrates. The results of these studies should provide guidelines for the selection of the best materials, processes and process controls for the production of good optical coatings for infrared components at wavelengths of 3-5 and 10.6 micrometers.

This phase of the work has centered on two different areas, while continuing the main work on antireflection coatings of cadmium telluride. An ion plating system was constructed, and more definitive work was done on the plasma polymerized films.

2. PREPARATION OF COATINGS BY ION PLATING

Ion plating is a vacuum coating technique in which a film is produced by depositing neutral atoms as well as ions on the substrate surface. There are two competing phenomena occurring at the surface of the substrate: the deposition of ionic and neutral species of the coating material; and the sputtering of the deposited film and substrate material by newly arriving ionic and neutral coating material species.

The substrate is placed at a high negative potential (V_s) with respect to the evaporating material; thus any positive ions formed will be accelerated toward the substrate. The high velocity of these incoming ions will generally cause them to be buried deeper into the surface than the neutral atoms. This, coupled with the competing sputtering process, leads to greater adhesion of the deposited film than when only netural atoms are deposited, even when a relatively small percentage of the coating species are ionized.

Apparatus and Procedure

A MRC electron beam zone refiner was modified for use in ion plating. Figure 1 is a schematic of the basic ion plating system. A tungsten filament was used as an electron source to evaporate the coating material. The coating material was placed on a pedestal, at a high positive potential (V_b); the electrons emitted by the hot filament were thus accelerated toward the material. A relatively high ion production can be achieved when an electron beam is used rather than joule heating. Biasing the substrate produces an electric field between the coating material and the substrate which augments the production of ions, as well.

By changing the filament current and V_b the evaporation rate of the coating material can be controlled. By changing the substrate-to-coating

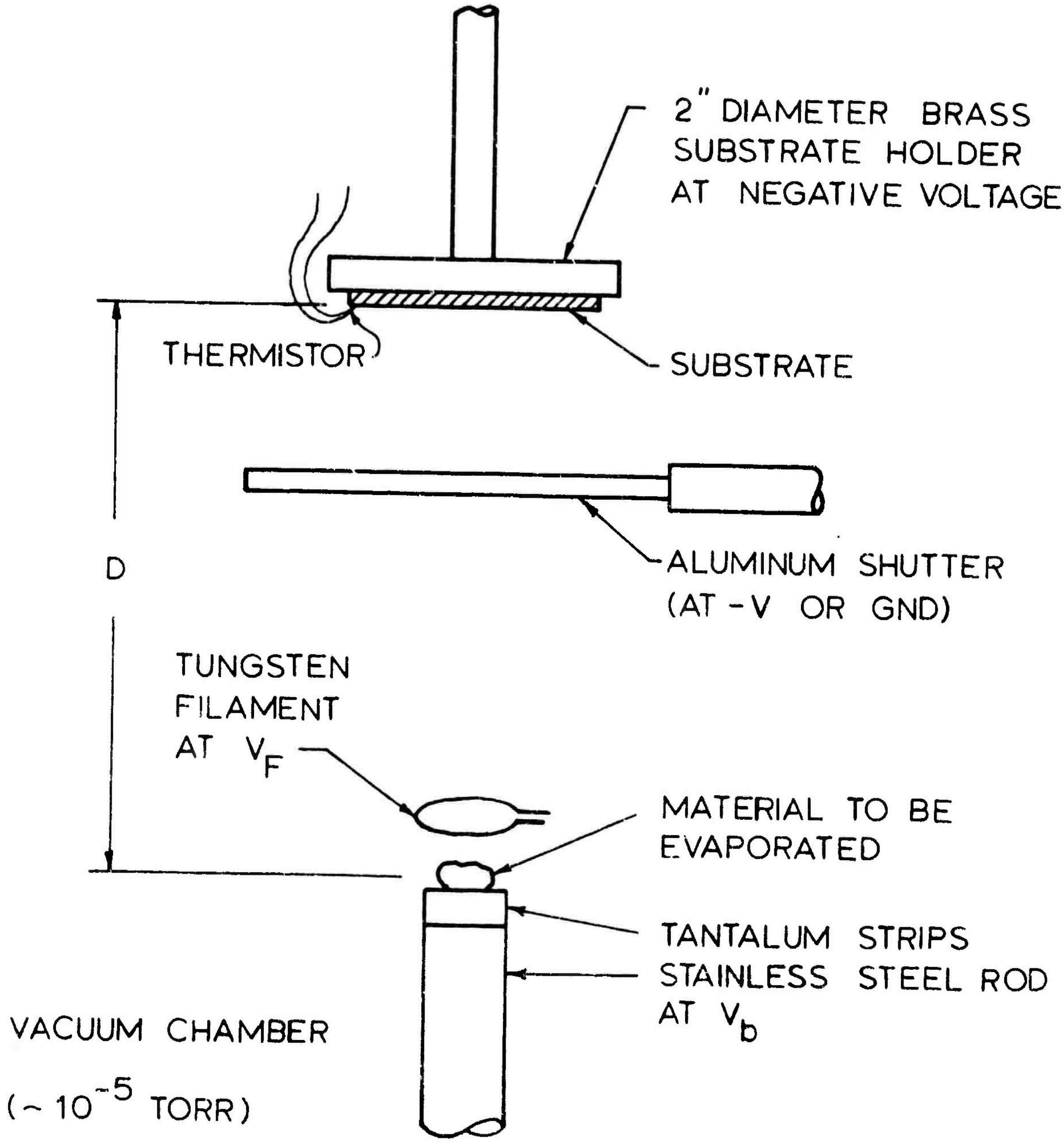

FIGURE 1
ION PLATING SYSTEM

material distance, D, one can control the ratio of ions/neutrals striking the substrate. Since the final velocity of the ions is a function of the potential difference between V_s and V_b, increasing V_s increases the velocity and hence the depth of penetration of the ions.

A thermistor located at the surface of the substrate was used to monitor the substrate temperature. A shutter was used to isolate the substrate while the coating material was being heated to a stable evaporation rate. Once a stable rate was achieved, the shutter was opened and plating allowed to take place until the desired thickness was obtained. The entire process was carried out in a vacuum chamber with a working pressure of between 10^{-4} and 10^{-5} torr.

Results

A number of germanium and cadmium telluride films were deposited on glass substrates. In addition, cadmium telluride was deposited on KCl substrates. The basic deposition parameters are shown in Table I. T_f is the final substrate temperature. Beam conditions refer to the electron beam used for heating and ionizing. The substrate-to-target distance is the measured distance between the surface of the coating material to be evaporated and the substrate surface.

Germanium films were prepared in an attempt to study the film-character of coatings prepared by different processes, since we have thoroughly studied sputter-deposited germanium films. The cadmium telluride films were prepared for simultaneous characterization with sputter-deposited films of the same composition. The ion-plated films have not been characterized as yet. However, the CdTe films appear very uniform and adhere extremely well both to glass and to KCl.

TABLE I. ION PLATED FILMS*

No.	Material	Substrate	T_f (oC)	Substrate Potential V_s (volts)	Ion Current (ma)	Filament Heating V_f (volts)	Filament Heating I_f (amps)	Beam Conditions V_b (volts)	Beam Conditions I_b (ma)	Substrate-Target Distance D (cm)
1	Ge	Glass	-	-1000	>25	6	22	-	-	14
2	Ge	Glass	-	-1000	>25	6	20	1000-1500	>0	10
[illegible]	Ge	Glass	-	-1000	>25	7	25	2000	150	10
6	Ge	Glass	43	-500	>25	6.5	22	1800	160	10
7	Ge	Glass	40	-500- -1500	>25	6-7	23-25	1800	150	10
11	CdTe	Glass KCl	60	-1000	4-7, >25	5.0	22-25	1400-2000	170-200	10
12	CdTe	Glass KCl	100	-500	8-9	4.0	21	2000	220	7

*Vacuum system pressure -5-x10^{-5} torr.

3. PLASMA POLYMERIZATION OF THIN FILMS:

Plasma polymerized organic films prepared as described in AFCRL-TR-75-0152 were submitted to Mr. Joseph Comer of AFCRL for electron microscope characterization, specifically by transmission electron microscopy and diffraction. The samples were prepared and examined by Mr. Comer using a JEM-6A electron microscope with a beam having an energy of 100 KV. He obtained electron micrographs for examining texture, selected area diffraction patterns, and high resolution electron diffraction patterns both to cover larger areas in diffraction and also to examine the films using a grazing incidence electron beam.

Two of the films were completely amorphous. Two of the films were highly crystalline but also showed the presence of an amorphous phase. Crystallite size was under 100Å. Textural differences were thought to be caused only by regions of different thickness.

The selected area diffraction patterns taken on the crystalline films could be interpreted as a cubic structure which could be indexed as diamond. Table II shows that the agreement with the diamond pattern is very good, although the measured values are close to certain reflections from graphite. A highly-oriented graphite film could produce a pattern with no 00ℓ reflection. To check for this the sample was tilted up to 20°, but no change in the diffraction pattern was recorded.

High resolution electron diffraction was used to confirm the selected area diffraction results. Table III shows the measured d-spacings for the same film as shown in Table II (SAD). Tilting the sample as much as 45° produced no change in the diffraction pattern. A glancing angle electron diffraction pattern was obtained from the same film (mounted on a grid) in an attempt to find an (00ℓ) graphite reflection. The results compared with an ASTM pattern for graphite are shown in Table IV. By this technique

TABLE II

Analysis of Selected Area Diffraction Patterns from Film No. 21, Plates 4590C and 4593C*

Measured d	Relative Intensity	Diamond (ASTM) d(Å)	hkℓ	Graphite (ASTM) d(Å)	hkℓ
				3.36	002
				2.13	100
2.06	vs	2.06	111	2.03	101
1.79	s	1.78*	200	1.800	102
				1.678	004
				1.544	103
1.26	m	1.261	220	1.232	10
				1.158	112
				1.138	105
				1.120	006
1.08	m	1.0754	311	1.054	201
1.03	w	1.03**	222	0.994	114,116
		.8916	400		
				.841	008
.82	vw	.8182	331	.829	116
				.801	211

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*J. Comer, AFCRL

**forbidden according to x-ray structure factor the (002), (006) and (008) reflections show up, indicating the possibility of graphite being present. However, the glancing angle diffraction pattern was obtained from only a small portion of the sample because of the distortion of the grid from previous measurements. If these films are graphitic, then they must be highly oriented with the c-direction normal to the surface of the film. On the other hand, if they are diamond (or diamond-like) as indicated by SAD and high resolution diffraction patterns from two different films, then this technique presents a new method for producing diamond-like films for protecting optical components. Further studies to elucidate this are being conducted utilizing electron microscope facilities at Penn State.

TABLE III

High Resolution Diffraction of Film No. 21*

Measured d (Å) (Pattern 4599C)	Diamond (ASTM)	
	d(Å)	hkℓ
2.06	2.06	111
1.795	1.78	200
1.265	1.261	220
1.082	1.0754	311
1.032		
	.892	400
.82	.82	331

*J. Comer, AFCRL

TABLE IV

Glancing Angle Electron Diffraction from Film No. 21*

Pattern 4604C d(Å)	Graphite (ASTM) d(Å)	hkℓ
3.36	3.36	002
2.12	2.13	100
	2.03	101
1.77	1.80	102
	1.678	004
1.30		
1.225	1.23	110
1.11	1.12	006
.84	.84	008
	.829	116
.79	.80	211

*J. Comer, AFCRL

4. AUTOMATED ELLIPSOMETER

The automated ellipsometer is nearly completed. Initial tests have been conducted and some design modifications made. Computer control has been established.

5. COMPUTER-CONTROLLED ELEMENTAL PROFILING WITH THE ION SCATTERING SPECTROMETER

The design and construction of interface equipment for linking the ion scattering spectrometer with a time-shared PDP-11/20 has been undertaken. This will allow completely automatic elemental composition profiles to be obtained with better accuracy than can be obtained with the normal manual control. Repetitive counting is being utilized to give better counting statistics, while the computer controls the channel, counting, and scan sequence. This feature, along with a newly-purchased beam-rastering and signal-gating unit will greatly enhance our compositional profiling ability, thus allowing more detailed studies of compositional changes and diffusion profiles in the coatings that are being characterized.

6. SPUTTER-DEPOSITED CADMIUM TELLURIDE FILMS ON KCl

Compositional profiles were obtained from CdTe films on KCl using ion scattering and Auger electron spectrometry. Although AES showed trace amounts of oxygen throughout the film, none was observed by ion scattering. In general, oxygen diffusion is unimportant in cadmium telluride sputter-deposited film. There may be some degradation with long-term exposure to air, however. The electron beam in AES does cause some problems, which are related to the alkali halide substrate. Other investigators[1,2] have reported diffusion effects when studying alkali halides by AES. The surface region becomes depleted of the halide leaving an alkali-rich surface. When a coating such as CdTe is placed on the alkali halide, the diffusional effects are still prominent. Chlorine comes through to the surface of the film, leaving a potassium-rich film-substrate interface. Another disconcerting fact appeared during these studies. Films prepared in two different sputtering apparatuses under identical conditions gave different compositional analyses. Amorphous CdTe prepared in the old MRC, oil-pumped unit was very cadmium rich, having a Cd/Te ratio of 2.5 (1.41 is stoichiometric). Amorphous films made under the same conditions in the turbomolecular-pumped Airco Temescal system (a "cleaner" system with a lower background pressure) were tellurium-rich, having a Cd/Te ratio of 1.05. More work must be done to elucidate this.

7. OXIDATION OF GERMANIUM FILMS

Compositional profiles of germanium films sputter-deposited on KCl substrates were obtained by ion scattering spectrometry. Previous studies were done on low density. amorphous germanium films. Other investigations[3,4] have suggested that low density amorphous films, as well as crystalline films, would be more susceptible to oxygen diffusion than high density films. Thus, further oxidation studies were done with high density germanium films. Ion scattering spectrometry was used to profile these germanium films for oxygen. Although oxygen was present throughout the film, it was found in significant quantities only in the 25Å or so of the film. Our data essentially confirms the AES results of others. As in the case of CdTe, we found chlorine diffused through the film to the surface.

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