PRODUCTION OF MULTICOMPONENT THIN FILMS
BY rf COSPUTTERING

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Ph.D. Thesis Submitted to Iowa State University

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Production of multicomponent thin films
by rf cosputtering

by

Barry F. T. Bolker

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ABSTRACT

A combination of rf cosputtering, film temperature control and film bias control has been investigated in the Te-As and Te-As-Ge systems to determine the feasibility of obtaining films of many different compositions from a single main sputtering target. Each of the techniques proved to be effective in influencing the film composition. An initial deficiency of Te observed in the films was attributed to the relatively poorer Te sticking coefficient. Ge was the cosputtered element, and it contributed theoretically predicted amounts of material to the films up to the 18 $\frac{1}{2}$ at% Ge level. Substrate temperature and substrate bias were seen to have a strong influence on the As/Te ratio of the films, and very little influence on the Ge content. The Te content of the films decreased for substrate temperatures between -150°C and 20°C, and then increased for temperatures between 20°C and 90°C. The temperature effect was caused by the change of the Te sticking coefficient with change in temperature. Application of an rf bias to the substrate caused a linear decline in the Te content of the films because Te preferentially resputtered from the film surface. This resputtering of Te confirms theoretical predictions. We found a simple linear relationship between the loss of Te in at% and the bias voltage.

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1 . INTRODUCTION

Rf sputtering is a particularly attractive method for the preparation of amorphous thin films of multicomponent samples. Almost all disciplines in materials science are studying such multicomponent samples. When the number of sample constituents exceeds two, the number of samples with different compositions required to study a physical phenomenon becomes large. The investigation then becomes expensive if individual sputtering targets of each composition are required. This thesis investigates the use of cosputtering together with control of film temperature and film bias to systematically prepare Te-As-Ge films over a considerable range of composition with a single main sputtering target.

A. Nature and History of Sputtering

In sputtering, high energy positive ions in a plasma discharge bombard a cathode target material and, by transfer of momentum, dislodge atoms or groups of atoms from this target surface. These ejected atoms can then be condensed on a substrate to form a thin film.

The first report of sputtering was in 1852 by Grove,¹ who deposited metal on the cathode of a glow discharge. Because a gas pressure between 10^{-3} and 10^{-1} Torr was necessary to maintain the plasma discharge, sputtering was considered a "dirty process" and films produced were often of an inferior quality. Vacuum evaporation of thin films, discovered by Nahrwold² in 1887, largely replaced sputtering during the first half of this century. Advances in vacuum technology, as well

as a better understanding of the nature and versatility of sputtering, have recently thrust sputtering into eminence for thin film fabrication.

One of the limitations on sputtering was that it could only be used for metals and some semi-metals owing to the fact that a dc voltage was used to maintain the plasma. The ion collisions with the target deplete electrons from the target surface. This depletion induces, on insulating and most semi-insulating materials, a surface charge layer that repels any further ions and effectively stops the sputtering process. To overcome this problem, Wehner,³ in 1955, and Anderson, Mayer and Wehner,⁴ in 1962, proposed the application of a high frequency potential to the cathode. In this manner, the surface charge caused by the bombarding ions would be neutralized every half cycle by electrons from the plasma. And since ion mobilities are orders of magnitude less than electron mobilities, there will still be a net acceleration of ions toward the target if the frequency applied is high enough, on the order of megahertz.³ This suggestion for rf sputtering was developed by Davidse and Maissel^{5a} in 1966 into a practical method for depositing films of insulating material. The operation of rf discharges and the internal distribution of voltages is discussed by Koenig and Maissel.^{5b} The standard frequency used is 13.56 MHz. Presently, almost any material can be sputtered. In fact, due to its very nature, sputtering can produce films unobtainable by any other method. Today, sputtering is widely used in both materials research and electronics manufacturing.

B. Te-As-Ge Chalcogenide Glasses

Sputtering is a particularly attractive method for the formation of amorphous materials because the high quench rate involved in the vapor-to-solid condensation permits a very wide range of compositions to be prepared in a non-crystalline structure, whereas bulk materials made by conventional methods such as splat-cooling usually have a crystalline structure.

Among amorphous materials, the chalcogenide glasses are of great interest due to their switching and memory characteristics.^{6,7} The switching characteristics of both thin film and bulk glasses have been extensively studied⁸ along with their other transport properties.

The Te-As-Ge system exhibits the characteristic properties of the chalcogenides. The bulk glass forming regions of the Te-As-Ge system were first investigated by Hilton⁹ and co-workers in their study of infrared transmitting glasses, and later by Savage¹⁰ in a survey on switching. Both studies showed that the bulk glasses formed predominantly at Ge compositions less than 20 at%. Switching in bulk samples,^{1,11} switching in thin films,¹² and other physical properties^{13,14,15,16} of this system have been examined in some detail. My own research group has investigated bulk sample preparation of various compositions of this ternary system¹⁷ and the visual switching effects of $\text{Te}_{73}\text{As}_{15}\text{Ge}_{12}$.¹⁸

This thesis investigates the preparation of amorphous thin-film samples in the Te-As-Ge system by rf sputtering techniques. A materials research approach is used in which one attempts to obtain

many different compositions in the system so that physical properties may be studied as a function of composition. The present work is concerned solely with the preparation of samples of Te-As-Ge with various compositions. Future work by others in the group will investigate the transport properties of these samples.

Basically, one wants to obtain as many different compositions as practical with the simplest target arrangement possible. Most previous sputtering work on binary, ternary, and quaternary systems has employed a single target of specific composition to produce a sample of that composition. When many compositionally different samples are needed, it becomes an expensive and time-consuming project to use a different target for each film. This problem can be partially overcome by cosputtering from two or more targets of different materials onto the same substrate. The deposited film will then contain a range of compositions, with each area of the substrate having its own composition.

The samples in this research were prepared by a special form of cosputtering which involved a main target - itself a homogeneous binary composition - and small subtargets or islands placed on the surface of the main target. The composition, placement, number, and size of these subtargets can be arranged to make predictable contributions to the stream of material arriving at the film under preparation.¹⁹ It was desired to produce thin films with a low Ge content so that future comparisons could be made between bulk material and the thin-film glasses. The best choice was to use Te-As as the main

target, and Ge for the subtargets. In this way, controlled amounts of Ge in the samples could be obtained.

It was also desired to vary the As/Te ratio in the films without changing the main target. Under normal steady-state sputtering conditions, the material arriving at the film has the same composition as the target. Control of the actual film composition then arises from control of those parameters which affect the incorporation of the sputtered stream of material into the film.²⁰ Three important mechanisms responsible for film compositions different from target composition are: (a) sticking coefficients which are different for different target constituents, (b) differential thermal desorption for the film constituents, and (c) differential resputtering from the film by bias sputtering. The first two of these mechanisms can be affected by varying the film temperature, the last by varying the bias conditions. So different substrate temperatures and different substrate biases were used in order to vary the As/Te composition of the films.

This thesis demonstrates that many different film compositions in the Te-As-Ge ternary system can be obtained from a single main target by employing a new approach that uses cosputtering, in combination with substrate bias control and substrate temperature control.

II. THEORETICAL CONSIDERATIONS

The usefulness of cosputtering is enhanced by the fact that film composition can be predicted for a well-defined target and substrate arrangement. The calculations have been reported by Hanak¹⁹ and co-workers, and will be briefly reviewed here.

The calculation of composition for multicomponent cosputtered films with constituents A, B, . . . J, . . . N is based on the superposition principle which states that the total film thickness $T_{AB \dots N}(P_O)$ at any point P_O on the substrate is equal to the sum of the individual film thickness $T_J(P_O)$ of each component. Each $T_J(P_O)$ can be expressed as

$$T_J(P_O) = t R_J(O') G_J(P_O) \quad (1)$$

where t is the sputtering time, $R_J(O')$ is the sputtering rate at some reference point (O'), and $G_J(P_O)$ is a geometry dependent deposition profile. Using this definition, the expression for the total thickness becomes

$$T_{AB \dots N}(P_O) = t \sum_{J=1}^N R_J(O') G_J(P_O). \quad (2)$$

In Eq. (2), t is known, $G_J(P_O)$ is calculable, and $T_{AB \dots N}$ are measured. The rates $R_J(O')$ can be calculated by solving N or more simultaneous equations. Once the rates are known, individual and total thicknesses anywhere on the substrate can be computed from Eqs. (1) and (2).

Film composition in terms of volume fraction $F_J(P_0)$ can be obtained from the expression

$$F_J(P_0) = \frac{T_J(P_0)}{\sum_{J=1}^N T_J(P_0)} \quad (3)$$

The deposition profile $G_J(P_0)$ is derived from Knudsen's cosine law emission²¹ and from certain other simplifying assumptions.¹⁹ For the case of rectangular coordinates, illustrated in Fig. 1, the deposition profile is

$$G(P_0)_{\text{rect.}} = \int_{y_1}^{y_2} dy \int_{x_1}^{x_2} dx \frac{D^2}{[(x-x_0)^2 + (y-y_0)^2 + D^2]^2}$$

The fundamental function for this double integral is

$$F_{\text{rect.}}(x, y) = \frac{1}{2} \left\{ \frac{x - x_0}{\sqrt{(x-x_0)^2 + D^2}} \arctg \frac{y - y_0}{\sqrt{(x-x_0)^2 + D^2}} + \frac{y - y_0}{\sqrt{(y-y_0)^2 + D^2}} \arctg \frac{x - x_0}{\sqrt{(y-y_0)^2 + D^2}} \right\}$$

Using this fundamental function, the deposition profile is rewritten as

$$G(P_0)_{\text{rect.}} = \int_{x_1}^{x_2} dx \int_{y_1}^{y_2} dy \frac{\partial^2 F(x, y)}{\partial x \partial y} = F(x_2, y_2) - F(x_1, y_2) - F(x_2, y_1) + F(x_1, y_1). \quad (4)$$

Fig. 1. Cosputtering geometry for rectangular coordinates.

In the above equations, (x,y) are coordinates of the subtarget location, (x_0,y_0) is a point on the substrate and D is the separation between target and substrate.

Equation (4) gives the distribution of sputtered material at a specific point on the substrate arising from a specific geometric arrangement of targets, subtargets, and substrates. For this thesis, a computer program was written to calculate deposition profiles for specific geometries and to predict the Ge content at desired locations on the film. One actual film composition was measured by the microprobe in order to fix the actual value of the Ge content at all other locations on the substrate. The Te-As main target was treated as one single material which comprised the remainder of the film composition. As will be discussed in the data section, the cosputtering equations did predict the relative Ge concentration for each of the three substrate locations examined. Hanak¹⁹ reported an average rms error of less than 10% in his work, and Hanak and Bolker,²² in extending the composition calculations to very dilute alloys, report an rms accuracy of 25%.

Early experimental evidence that an applied bias affects the film properties was reported in 1964.^{23,24} This early work dealt with the ability to change a film's electrical resistivity through the use of an applied negative dc bias. The bias led to a resputtering of the film's surface with a preferential removal of impurities relative to the atoms of the main film.²⁵ Reviews on the control of the properties

of sputtered film can be found in the articles by Maissel,²⁵ Christensen,²⁶ and Vossen.²⁷

More pertinent to this thesis are reports that the relative composition of multicomponent films can be influenced by an applied bias. According to Winters²⁰ and co-workers, the reason for the compositional changes is that the applied bias will cause a resputtering of the film, with some of the constituent material being preferentially resputtered. They suggest that this preferential resputtering will be a strong function of the relative atomic sizes of the film constituents. They even predicted that by changing bias, it should be possible to grow a series of films with different compositions using the same target. Evidence for a compositional change due to applied bias was reported recently for the GeTe_2 system.²⁸

In some very recent work, Cuomo and Gambino²⁹ reported compositional changes due to applied bias in the Gd-Co, Gd-Co-Au, and Gd-Co-Mo systems. More interesting is a semi-empirical equation that they have developed which relates actual film composition to the target composition, using geometry and system potentials as parameters. Making certain assumptions, they obtain for the Gd-Co system a relation which predicts the effect of bias on the film composition

$$\left(\frac{\text{Co}}{\text{Gd}}\right)_{\text{film}} = \left(\frac{\text{Co}}{\text{Gd}}\right)_{\text{target}} \left[\frac{1}{1 - K \left(\frac{V_b}{V_t}\right)} \right] \quad (5)$$

where $(\text{Co/Gd})_{\text{film}}$ is the film composition, $(\text{Co/Gd})_{\text{target}}$ is the target composition, K is a constant factor depending mostly on system

geometry, V_b is the effective bias potential, and V_t is the target potential. The factor K is a fitting parameter which gives the best fit for a series of films done with different biases but under the same geometric conditions. The present Te-As and Te-As-Ge data are examined in Section VII to see if this equation can predict the effect of bias on the film composition.

III. SPUTTERING APPARATUS

A. Sputtering Module

Thin-film samples were produced in a radio frequency (rf) sputtering unit built by Ion Equipment Corporation. The unit was coupled to a vacuum system and baseplate designed by me and built by the Ames Laboratory shops. Figure 2 shows the installed system. The height to the top of the module is 2 m (6.5 ft.) and the bell jar is 61 cm (24 in.) in diameter.

A close-up of the sputtering module in the open position is shown in Fig. 3. Located at the stainless steel top plate are three target holders 120° apart (two are visible in picture). Two of these holders are for permanent targets, and the whole holder must be removed to change targets. The third holder has a removable bottom plate to facilitate the changing of targets. All the holders are internally cooled by water and all will accept standard-sized targets of 15 cm (6 in.) diameter.

A movable pedestal (or "J") can be positioned by rotation to lie beneath any one of the three targets, or beneath one of the three positions between targets. The height of the pedestal can be changed, thereby allowing variation in the target to substrate separation. The pedestal is internally water cooled. All linear motion and rotation occur through differentially pumped O-ring feedthroughs.

The stainless steel plate nearest the targets serves as a shutter. It has one opening which can be positioned between target and substrate so that deposition will occur. The lower stainless steel plate contains

Fig. 2. Rf sputtering system. Power supply is at far left, next to Roots pump. Tuning network is located atop the glass bell jar. Diffusion pump is at far right. Instrument rack contains vacuum monitoring equipment.

Fig. 3. Close-up of sputtering module in open position showing details of sputtering chamber. Film thickness monitor can be seen at shutter opening. A Te-As main target is mounted on pedestal for "sputter-up" configuration.

six holes which accept substrate platens. Overall, the system has the capability of sputter depositing three different materials onto six different substrates without breaking vacuum. The sputterings can be done in any order, and, of course, multiple depositions on a single substrate can be achieved.

The upper encased part of the module, which is outside the vacuum, contains an rf matching network (inductor and capacitor) plus voltage and height meters, and selectors for choosing the appropriate target and substrate positions. Some additional feedthroughs have been installed in the top plate to provide vacuum access for thermocouples, heaters, and other desired instruments.

Power is supplied by a one kilowatt rf generator manufactured by Henry Electronics (seen at far left of Fig. 2). Output frequency is crystal controlled at 13.56 MHz. The generator, as received, incorporated high-voltage safety interlocks for the cabinet door and for the air cooling fans. However, there was no safety interlock for the water cooling, so a flow switch was installed in the water line. In case anything should happen to the water cooling, the power will cut off, preventing the heating, warping, and possible destruction of targets or substrates being sputtered.

B. Vacuum System

The facility has a dual pumping system consisting of a 10 cm oil diffusion pump for high vacuum clean-up and a large mechanical Roots pump (oil free) for high throughput during sputtering. Figure 4 shows schematically the vacuum system, and most of the parts can also be

Fig. 4. Block diagram of vacuum and gas-flow systems.

seen in Fig. 2. The pumps are located on opposite sides of the base-plate and all connections are made with stainless steel.

A 15 cm (6 in.) Veeco manually operated butterfly valve with viton seals provides access to the high vacuum pump. A Granville-Phillips 15 cm (6 in.) LN_2 cold trap and an optically dense chevron baffle prevent oil from back-streaming into the system. The High Vacuum Equipment Corporation 10 cm (4 in.) diffusion pump is backed by a Welch model 1397 forepump. This forepump also evacuates the differentially pumped O-ring seals of the sputtering module. After two hours bake-out at 150°C , the chamber can reach a minimum pressure of less than 1×10^{-7} Torr. In routine use, without bake-out, the chamber can reach the low 10^{-7} Torr pressure range after about 1.5 hours. All of the samples have been prepared in this latter manner, with the chamber reaching a clean-up vacuum with a pressure of 2×10^{-7} Torr before sputtering began.

The Hereaus Roots pump type RG1000 employs two close fitting figure-eight cams to pump large quantities of gas without the use of oil. This pump is connected to the chamber by a Torr Vacuum Products 15 cm (6 in.) right angle valve with welded bellows stem seal and viton gate seal. Beneath the Roots pump is a cold trap of my own design which prevents sputtering by-products and contaminants from reaching the environment as well as keeping forepump oil from entering the system. A Hereaus type E225 single-stage mechanical forepump backs the Roots pump. A metering valve, installed in the forepump line, was adjusted to keep 100 μm pressure in this line. At this pressure, a laminar flow of

particles was moving toward the forepump and was a further guard against any oil back-streaming into the system. During sputtering (pressure $\sim 20 \mu\text{m}$), with the right angle valve fully open, this pumping system has a throughput of $140 \text{ Pa}\cdot\text{l/s}$ ($1.1 \text{ Torr}\cdot\text{l/s}$). The high throughput was necessary so that the sputtering plasma could be constantly renewed and any sputtering contaminants or by-products could be swept away. In this vacuum chamber, with a volume of 185 l , the plasma was renewed once every 4.4 seconds when sputtering at $20 \mu\text{m}$.

A diffusion pump cannot operate efficiently in the $5 - 70 \mu\text{m}$ range needed for sputtering.³⁰ Thus, in a conventional pumping system employing only a diffusion pump, the pump orifice must be partially closed during sputtering. This closure necessarily limits the throughput. My dual system offers both excellent high vacuum clean-up and high sputtering throughput. Quite independent of my own work, Bell Telephone Laboratory has reported some sputtering results in a system that employs this same dual pumping method.³¹

In actual operation, after loading the samples and closing the top plate, the right angle valve was opened, and the Roots pump was used to evacuate the chamber to the 10^{-3} Torr range. Then, the right angle valve was closed and the butterfly valve was opened so that the diffusion pump could begin the clean up. When the pressure was in the low 10^{-7} Torr range, the diffusion pump was closed off, argon gas was admitted to the chamber, and the Roots pump orifice was opened. Even when closed off, the diffusion pump was kept operating and an automatic filling system was used to keep its LN_2 cold trap filled.

The sputtering atmosphere (argon gas of 99.99% purity) was admitted to the chamber by opening a stainless steel toggle valve. The argon flow was precisely controllable through the use of a Nupro needle valve with a vernier metering scale. The rate of flow was continuously monitored by a Hastings mass-flow meter. Normally, the desired gas pressure for sputtering was obtained by adjusting the inlet needle valve and having the right angle valve to the Roots pump fully open. Lower throughput (that is, lower flow rate) could be obtained by partially closing the right angle valve - in effect, throttling the Roots pump - and correspondingly adjusting the inlet needle valve.

A back-to-atmosphere line was provided so that the chamber could be pressurized with dry nitrogen gas before opening. Both this nitrogen line and the argon line are schematically shown in Fig. 4.

The baseplate is a 61 cm (24 in.) diameter by 30.5 cm (12 in.) deep stainless steel chamber of my own design which provides 13 equipment access ports in addition to the two pumping ports. On the baseplate wall are located ten 3.8 cm (1.5 in.) diameter ports, sealed by Ultek copper seal flanges. Four of these ports are presently being used for vacuum gauges and heater lead feedthroughs. The remaining six are for future use. On the baseplate bottom are three additional ports, two of 3.8 cm (1.5 in.) diameter and one of 15 cm (6 in.) diameter. These three ports are located directly below the three target locations and are available should a lifting pedestal or in-situ measuring equipment be needed. In addition, the 15 cm (6 in.) diameter port will accept a standard turbo-molecular pump.

On the inside walls of the baseplate are two Conax 1.5 m (60 in.) resistance heaters which are used to bake out the chamber. These heaters use #24 gauge Nichrome wire in a stainless sheath. They are designed to reach a temperature of at least 300°C. During an actual bake-out, using half power, the sheath temperature was measured at 560°C. This temperature was sufficient to heat the baseplate walls above 100°C and out-gas water vapor in the chamber. Although the bake-out heaters have not been needed frequently, they do provide sufficient power to de-gas the vacuum chamber adequately.

C. Monitoring Equipment

A mass-flow meter was used to monitor the rate of flow of argon gas entering the sputtering chamber. For most of the sample runs, this flow rate was a constant 65 standard cubic centimeters/minute. The mass flow gives an indication of how much gas was being swept through the chamber, but the actual pressure inside the chamber was measured by three different types of vacuum gauges.

A thermo-gauge tube connected to a Granville-Phillips series 224 gauge controller read pressures between atmosphere (~ 780 Torr) and 10^{-3} Torr on one non-linear scale. One thermo-gauge tube, located in a baseplate port, was used mainly during pump down with the Roots pump to indicate when the pressure was low enough to open the butterfly valve to the diffusion pump. A second thermo-gauge tube has been placed in the pumping line between the Roots pump and its forepump. This gauge was used in conjunction with a variable leak needle valve to insure that the foreline pressure was approximately 100 μ m. Maintaining

this 100 μ m foreline pressure insured a laminar flow region and prevented oil from back-streaming to the Roots pump.

As soon as the system had been switched to the high vacuum mode, pressure was measured by a Bayard-Alpert ionization gauge connected to a Veeco RGLL-6 ionization gauge controller. The controller read from 10^{-2} Torr to 10^{-12} Torr in linear decade ranges. There were two Bayard-Alpert gauges in the system, one in a baseplate port, and the other in the butterfly valve. Either gauge could be used to measure the chamber pressure. The second gauge, located near the diffusion pump orifice, would at lowest pressures typically read 50% lower than the first gauge which was located across the chamber from the diffusion pump. In addition, the second gauge was located on the diffusion pump side of the butterfly valve, so that when the chamber was closed off, this gauge could measure the ultimate minimum pressure of the diffusion pump.

In combination, the thermo-gauge and the Bayard-Alpert gauge spanned the whole vacuum range of interest. But neither of these gauges would operate in the presence of the rf sputtering plasma. In order to measure pressures during sputtering, a Schulz-Phelps gauge tube with radio frequency interference shielding was needed. Plugged into the Granville-Phillips series 224 gauge controller, this Schulz-Phelps gauge tube read pressures from 1 Torr to 10^{-6} Torr in 6 linear decade ranges. Practical lower limit was about 10^{-5} Torr due to background cosmic radiation, but it performed very well in the 10^{-2} and 10^{-3} Torr ranges required for sputtering. This gauge, too, was located on one of the baseplate ports.

In addition to flow and vacuum measuring devices, this sputtering facility incorporated a new, experimental film thickness transducer built by Kronos-Veeco. Like conventional thickness monitors, this model FTT-400 transducer measures the shift in period of a quartz crystal oscillator due to a build-up of deposited material on the crystal surface, and then converts this period change into a thickness. However, conventional transducers cannot operate in an rf plasma environment. This new model has a remote 5MHz sensor to excite the crystal. This oscillator can be placed outside the chamber and thus away from the rf interference. In my system, the remote sensor was placed on the top plate of the sputtering module and was connected to the transducer crystal with shielded coaxial cable. Additionally, the transducer incorporates a magnet near the quartz crystal surface so that the electrons present in the plasma can be deflected, thus preventing the crystal from heating up.

The thickness monitor faced the target, and was mounted next to the substrate holder. Combined with a Kronos QM-2 Digital Thickness Monitor, the FTT-400 could measure up to the equivalent of 200,000 Å of aluminum in three ranges: 0-2,000 Å, 0-20,000 Å, and 0-200,000 Å. To test the accuracy of the thickness monitor, some tests with sputtered aluminum were made. The film thickness monitor indicated a thickness of 1560 Å. The average film thickness as determined by a Varian Å-Scope Interferometer was 1588 Å. The error, then, was less than 2%.

The thickness monitor was employed so that films of about 1 μm in thickness could be made. This 1 μm was the minimum thickness needed for

accurate compositional analysis by the electron microprobe. In actual practice, the thickness monitor was used to determine the amount of time (that is, sputtering rate) needed to deposit a 1 μ m film. Once this time was established, the thickness monitor became a secondary factor, and in fact, in many of the later runs, the monitor was not used at all.

There are some disadvantages in the use of such a monitor. One is that the sensor head - 3 cm (1.2 in.) in diameter and 1.3 cm (0.5 in.) high - will, by its physical presence, distort the plasma field. Thus, the head cannot be placed too close to the samples without danger of introducing distortion in the plasma and perhaps affecting the properties of the film. Also, the thickness monitor has no way to account for the effect of bias on the films being deposited. With a bias applied, some of the film material is resputtered, but there is no way to apply a bias and get this same resputtering from the crystal of the thickness monitor. Under bias conditions, the monitor will indicate a film thickness greater than the actual value. In my work, these factors were realized, and it was found that the thickness monitor was a reliable way to monitor sputtering rates and to achieve desired film thickness under non-bias conditions.

D. Substrate Holder

Substrate temperature was an important parameter in the present experiments, and it was necessary to have a substrate holder which could provide a wide range of temperatures. The requirements of cosputtering necessitated the use of a "sputter up" configuration; that is, the target resting on the "J" with the sample substrates above it. The substrates

could have been positioned on what was previously called a target mounting plate. But these target holders had provision for water cooling only, so this would have severely limited the obtainable substrate temperature range. The special substrate holder shown in Fig. 5 was designed to provide the temperature range needed. This stainless steel holder, 15 cm (6 in.) in diameter, had the same external dimensions as the target holder which it replaced. The water line, coolant line, and center cylinder came through the top plate of the sputtering module and are in air. The rest of the holder is inside the vacuum chamber. Sealing is by means of a viton O-ring. Substrates were mounted on the bottom plate of the holder. A water chamber, accessed by a stainless steel water line (only one shown), allows room temperature water to flow in the area beneath the O-ring groove. This water circulation protects the O-ring from the temperature extremes experienced at the bottom plate of the holder, thereby insuring the integrity of the vacuum seal.

A stainless steel coolant line and a stainless steel-sheathed resistance heater were silver soldered to the bottom plate of the holder. The stainless steel coolant line (only one shown) is 0.5 cm (0.1875 in.) in diameter and has a double-walled vacuum construction at the point where it enters the interior of the holder. Water, liquid nitrogen, and cold nitrogen gas have been used in the coolant line to maintain the holder (and substrates) at various temperatures between 20°C and -150°C. The heater element is essentially the same as the bake-out heaters used for the chamber. The total length of this heater is 1.06 m (42 in.). It is

Fig. 5. Design details of substrate holder.

designed to reach a sheath temperature of 450°C when operated at 120 volts. In the present experiments, the heater has been used to attain substrate temperatures above room temperature to about 100°C .

In order to measure the temperature of the bottom plate, two chromel vs alumel thermocouples were also soldered to the plate. The thermocouple wires are insulated inside the chamber with ceramic fish spine beads to prevent shorting. The thermocouple leads as well as the heater are vacuum sealed with Conax glands not shown in Fig. 5. Also provided on the holder is a vacuum line so that the interior can be evacuated. Evacuating the holder prevented condensation from occurring when cold liquids were run through the coolant line, and reduced convective heat losses when the heater was operating. The very thin (0.08 cm) vertical walls of the holder served to reduce conductive heat leaks between the bottom plate and the upper levels of the holder. A final detail not shown in Fig. 5 is the six screws which were used to mount the holder into the sputtering module top plate.

IV. SAMPLE PREPARATION

A. Target Fabrication

It was desired to have a sputtering target with high Te content, and all the samples prepared for this project come from a $\text{Te}_{75}\text{As}_{25}$ main target. In the course of gaining experience in target fabrication, a variety of techniques were tested and a number of targets, all with between 70 at% and 80 at% Te, were made. Because Te and As in these proportions are mutually soluble³² and melt below 400°C ,^{33,34} it was decided to prepare the target by melting the powders of Te and As in a medium-temperature furnace. This furnace is shown in Fig. 6. The 30.5 cm (12 in.) diameter stainless steel bell jar is water cooled, can be evacuated, and has a 5.4 cm (2 in.) diameter view port. To this bell jar was added an aluminum baseplate with viton O-ring seal. Power was provided by a 750 watt disc-shaped resistance heater of the type used on diffusion pumps. The baseplate was insulated from the heater by a 6.4 cm (2.5 in.) high ceramic standoff, and a 0.64 cm (0.25 in.) thick copper plate on top of the heater provided uniform heat distribution. Heater temperatures were measured with a chromel vs alumel thermocouple. During target melting, the target mold was placed on top of the copper plate, with the thermocouple wedged in a V-groove between the mold and plate. A pumping line ran from the aluminum baseplate to a Welch model 1405 pump. A Hastings Thermo-Gauge, type DV-3M, located in this pumping line, measured the furnace pressure.

It was desired to melt the target either in vacuum or under an inert atmosphere so as not to introduce any contaminants into the material.

Fig. 6. Furnace for producing Te-As main targets.

During an initial test melt with the furnace evacuated to $10\text{ }\mu\text{m}$, the arsenic evaporated instead of melting. A check of the handbook³⁵ indicated that pressures near atmosphere would be needed to keep the arsenic from subliming. Argon was then chosen as the inert atmosphere since the sputtering atmosphere would also be argon. In view of the fact that argon from the sputtering environment could be expected to be incorporated into the film samples,²⁵ it was assumed that any argon incorporated into the target during melting would not additionally affect resultant films.

A number of different materials were employed as molds for the target. Initially, pyrex evaporation dishes were used as molds. The pyrex molds produced some satisfactory targets in an experimental 7.6 cm (3 in.) diameter size. But in the larger 14 cm (5.5 in.) size needed for the actual target, the pyrex was prone to thermal stresses and to uneven heating. A number of attempts to melt in these pyrex molds ended in failure, either because the powders did not melt completely or because the mold cracked.

Next, a machined stainless steel mold was tried. Though this mold provided a satisfactory target from the standpoint of melting, it was discovered that the Te of the target material was reacting with the nickel in the stainless steel. Further investigation showed that Ni formed a eutectic with Te at 99.7 at% Te at a temperature $1\text{ }^{\circ}\text{C}$ below the melting point of Te³⁶ (449.5°C).

Successful targets were finally produced in molds of pure iron, since Te does not diffuse into Fe even at 1000°C and the solubility of

Te in solid Fe is very small.³⁷ Although arsenic and iron can react when heated together at 470°C for several weeks,³⁸ no reaction was observed in the present case, probably because the heating time was on the order of 30 minutes. The iron mold was machined from a 14 cm (5.5 in.) by 0.64 cm (0.25 in.) high disc of Armco Iron. The actual target was 13.7 cm (5.375 in.) in diameter by 0.32 cm (0.125 in.) thick.

The main target was fabricated from 99.9999% purity Te and As (Cominco-American, Inc., Spokane, Wash.). The Te came in the form of pellets about 3 mm wide and was used as received. The As was supplied in chunk form, and these chunks were crushed to approximately the same size as the Te pellets before being melted. The procedure followed was to weigh out the required quantities of Te and As, mix the material together in a container, and then pour it into the mold. After positioning the mold on the heater, the furnace was sealed and then evacuated to about 50 μ m by the pump. Argon was then admitted to the furnace and pumped out. After three such flushings, the pump was closed off and argon was back-filled into the furnace until atmospheric pressure was reached. The heater power was then applied, raising the mold temperature to 440°C within half an hour. This temperature was maintained for about 20 minutes, during which time all the Te and As could be seen to melt and become liquid. Power was then turned off and the target was allowed to cool.

The target remained in the mold, and the mold itself was cemented to the sputtering chamber "j" with a silver-loaded epoxy, Eccobond Solder 59 (Emerson & Cuming, Inc. Northbrook, Ill.). A grounded stainless steel guard

ring was used for all sputtering runs. This guard ring limited the effective sputtering diameter of the target to 12.7 cm (5 in.) and thereby eliminated any possibility that the iron rim of the mold would sputter and deposit onto the samples.²⁵

Electron microprobe analysis of the Te-As target showed it to consist of small-grain As_2Te_3 in a Te matrix. Homogeneity of the $\text{Te}_{75}\text{As}_{25}$ target was verified by sputtering it onto a 3" X 3" substrate. A complete microprobe analysis of this substrate indicated a very homogeneous film, from which it is concluded that the target itself was of uniform composition.

The subtargets used in these experiments were 0.04 cm (1/64 in.) thick slices of semiconductor grade Ge (Eagle-Picher Chemical Co., Cincinnati, Oh.) physically resting on top of the Te-As main target and held in place by gravity. The slices were 1 cm (0.4 in.) by 3 cm (1.2 in.) in size, and were positioned on the main target to give a desired Ge content to the films as determined by the equations of Section II. These pieces were sliced off a Ge bar using a diamond saw, and were etch-cleaned in an acid solution of 1.0 part HF:1.0 part Acetic:1.6 parts HNO_3 before being sputtered.

B. Substrates

The substrates in these experiments were standard 1.3 cm X 1.3 cm X 0.08 cm (0.5 in. X 0.5 in. X 0.031 in.) Corning 7059 glass with a typical surface smoothness of 1/2 microinch (manufacturer's figure). This size substrate was chosen because it would conveniently fit the mounting holders of the electron microprobe. Before being mounted

in the sputtering chamber, the substrates were blown off with dry air and then vapor degreased in isopropyl alcohol in accordance with the manufacturer's recommendations. To insure good thermal contact with their holder, the substrates were coated on the back side with a Ga-In eutectic.

In most runs, three individual substrates were used so that three different Ge-composition films would be produced. The position of the substrates in relation to the target is illustrated in Fig. 7. The center substrate was located at the middle of the substrate holder, and the outer substrates were each 4.4 cm (1.75 in.) from this center. A removable aluminum cover plate, with holes at the substrate locations, was placed over the substrate holder bottom plate so that deposition would occur only on the substrates and not build up on the remaining area of the holder plate. The substrates themselves were fastened to the holder plate by means of stainless steel tension clips. In addition, the center substrate had provisions for a special holder which incorporated contacts for the temperature sensor that will be described in Section V.

C. Sputtering Parameters

The effects of substrate temperature and substrate bias on film composition were the main sputtering parameters investigated in this research. It was necessary, therefore, to maintain other parameters such as pressure, throughput, power level, target distance, and film thickness at constant values.

Fig. 7. Target and substrate arrangement:
 (A) Top view showing substrate locations in relation to the Ge subtargets.
 (B) Cross-sectional view of Fig. 7(A). The substrate holder plate is the bottom part of the substrate holder shown in Fig. 5.

As previously discussed, the vacuum gauges and mass flow meter together with the calibrated needle valve enabled constant and repeatable vacuums and throughputs to be maintained. For most of the samples, the argon pressure was 2.7 pascal ($20\text{ }\mu\text{m}$ of Hg) and the throughput was 140 Pa-l/sec (1.1 Torr-l/sec). This 140 Pa-l/sec throughput was the maximum obtainable at the 2.7 pascal pressure. Three runs were made at lower throughputs by throttling the Roots pump. With throughputs as low as 35 Pa-l/sec (0.28 Torr-l/sec) there was no significant change in sample composition.

Pressure changes can be expected to alter the film composition^{25,26} because a change in argon density would affect the number of particle collisions and the scattering at the particles within the plasma. Typically, a higher pressure would result in more collisions for the sputtered material with an increased probability that the sputtered species would escape the plasma and be lost to the chamber walls or fixturing. Additionally, sputtering pressure can influence the accumulation rate of material at the film surface. At lower pressure, less sputtered material is lost from the plasma and hence more of the sputtered species deposits on the sample. The 2.7 pascal ($20\text{ }\mu\text{m}$) argon pressure utilized was empirically chosen to provide a steady, stable plasma and to allow an acceptable sputtering rate.

Pressure effects were not investigated in the present experiments, mainly because the cosputtering equation (Eq. 2) in Section II does not include sputtering pressure as a parameter and requires that all runs be done at the same pressure. Additionally, it was felt that both Te

and As ejected from the main target would experience similar collision processes as the pressure changed, resulting in a As/Te ratio that would not be significantly altered. This reasoning does neglect the fact that the sputtered species had different sizes and masses which would have led to preferential losses of certain species if the pressure were varied.

The films were sputtered at 200 watts total rf power as measured on the output meter of the rf generator with the system adjusted to peak tune. This power level provided a reasonable sputtering rate while avoiding the problem of excess target heating. As in the case of pressure, variations in power level have been reported to cause changes in film composition.²⁵ Some samples were made at 50W and 100W as well as at 200W, and minor compositional changes were observed.

The bias applied to the samples was an rf bias obtained by using the power splitting feature of the system. The output power of the generator could be split and applied to both target and substrate by means of a tunable coupling capacitor. When the capacitor was fully coupled to the pedestal, all the generator output was supplied to the target. The voltage between target and ground was 800V at 200W output. The substrate had no applied bias and was additionally grounded by a clip lead to prevent any induced bias. This set of conditions was called 0% bias. As the plates of the coupling capacitor were rotated, power was diverted from the target to the substrates. At the condition of 20% bias, there was approximately 600V on the target and 150V on the substrates, both with respect to ground.

The effect of the substrate bias was to cause bombardment of the substrate film by the argon ions and resulted in a resputtering of the film material. Most reported bias work employs a dc bias. Rf bias is comparable to a negative dc bias since both result in the bombardment of the film by positive argon ions.

The separation between target and substrate was maintained at a constant distance of 4.8 cm (1.875 in.). All samples were sputtered for 30 minutes or longer to achieve a film thickness of $1\mu\text{m}$ or greater. The actual height of the film was not considered important as long as the film was thick enough to prevent breakthrough by the electron beam during microprobe analysis.

V. TEMPERATURE OF SUBSTRATES

The effect of film temperature during deposition on film composition was an important part of this research. It was desired to reliably measure the actual surface temperature of the substrate, and this requirement led to the development of a thin-film platinum resistance thermometer. The chromel vs alumel thermocouples on the bottom plate of the substrate holder were adequate to measure the bottom plate temperature, but the need to know substrate surface temperatures necessitated a sensor on this surface. Methods employing a wire thermocouple or some type of bulk resistance sensor were judged to be undesirable in that the physical size might cause plasma distortions and the thermal bonding to the surface might introduce temperature uncertainties. A thin-film temperature sensor, intimately deposited on the substrate surface, would overcome these disadvantages. The choice, then, was between a thin-film thermocouple and a thin-film resistance thermometer.

Early work by Burger and van Cittert³⁹ involved evaporated thin-film thermocouples of Bi-Sb, while Harris and Johnson^{40,41} studied dc sputtered Bi-Sb and Bi-Te thin-film thermocouples. More recently, evaporated thin-film thermocouples of Fe-Ni,^{42,43} Cu-Fe,⁴³ Cu-Ni,⁴³ Au-Ni,^{44,45} Ag-Bi,⁴⁶ and metal-metal alloys^{43,47} have been reported. Messier⁴⁸ recently described a sputtered thin-film Ge resistance thermometer for measuring substrate surface temperature.

It was decided to sputter a thin-film Pt resistor onto the substrate surface and use it as a temperature sensor. Platinum resistors have long

been used for temperature measuring devices and are known to be stable and accurate. In the temperature range of interest (-200°C to $+150^{\circ}\text{C}$), the Pt resistance vs temperature curve is approximately linear, so that calibration of the sensors could be readily done using a few reference points. In addition, platinum could be conveniently deposited in the sputtering apparatus. A previously reported problem⁴⁹ concerning the adhesion of platinum films to glass substrates was not encountered in these thermometers.

Together with the actual resistor, provision was made on the substrate for contacts to the resistor and for protective insulation over the top of the resistor. All materials were sputtered onto the substrates, and the sequence of deposition is shown in Fig. 8. The serpentine platinum resistor (A) was 0.13 mm (5 mil) wide and approximately $1500 \text{ \AA}$ thick. Next, Mo for contact pads was sputtered to a thickness of $7000 \text{ \AA}$. The additional contacts on the left side of (B) were provided for later four-probe resistivity measurements on the samples. Molybdenum was the best material for contacts since Mo is stable in air⁵⁰ and forms non-injecting contacts with the chalcogenide glasses.^{51,52} A $3200 \text{ \AA}$ thick layer of SiO_2 was sputtered over the resistor (C) to prevent shorting of the elements. SiO_2 also served to passivate the material it covered.⁵⁰ Finally, provision was made for a sample mask (D) so that the sputtered film would be deposited over the resistor and also in a separate well-defined area to be used in resistivity measurements. However, for all the films in this experiment, no sample mask (D) was used since only film composition was being studied.

Fig. 8. Mask detail for thin-film thermometer:

- (A) Platinum resistor for temperature sensing.
- (B) Molybdenum contacts to resistor and for four-probe resistivity measurements.
- (C) Silicon dioxide protective covering over resistor.
- (D) Sample area for resistivity measurements. This step was not used in the present work.

In order to get the well-defined patterns of Fig. 8, the materials were sputtered onto the substrates through masks of etched Mo sheet. Thirty-six thermometers were prepared at a time, requiring the use of 10 cm X 10 cm X 0.076 mm (4 in. X 4 in. X 3 mil) Mo sheets for each mask. Photo fabrication techniques⁵³ using Kodak Thin Film Resist (KTFR) were employed to produce these masks. The KTFR was first thinned to a viscosity of 50 centipoise. Then the Mo sheets were dipped into the resist and withdrawn at a controlled rate. After drying, the sheets were exposed to the pattern negatives, in vacuum and under Hg vapor lamps, for 2 minutes. After developing, the sheets were acid etched (1 part HNO_3 : 1 part H_2SO_4 : 3 parts H_2O) in order to cut the pattern through the sheet, and the remaining resist was stripped off.

The masks (A), (B), and (C) were successively positioned over a 6 X 6 array of the substrates and the required depositions were performed. After each run, the vacuum had to be broken in order to change the masks. The yield for the thermometers was 1/3 to 1/2, due mainly to contact problems between the mask and the substrates. During deposition, the masks heated up, and thermal expansion of the Mo caused the masks to lift out of contact with some of the substrates. This lifting led to a fuzziness in the fine lines, especially during the Pt resistor deposition, and caused a subsequent rejection of some of the thermometers. After these three depositions, the completed thermometers were annealed at 160°C for 24 hours. They were then stored in a vacuum desiccator until needed.

Before use, each thermometer was individually calibrated at three known points: acetone and CO_2 (-60°C), ice and H_2O (0°C), and room temperature (25°C).

The actual temperature of the acetone- CO_2 bath was determined by a chromel vs alumel thermocouple. Mercury bulb thermometers were used to ascertain the exact ice bath and room temperatures. These three points defined a straight line on the temperature vs resistance graph, and actual film temperatures during deposition were interpolated from this graph. When the sensors were to be used for runs outside this temperature range, additional calibration points were added. For low temperature runs, the sensor was checked at liquid nitrogen (-196°C). For temperatures above 25°C , the sensor was calibrated in an oven ($50^\circ\text{C} - 100^\circ\text{C}$) whose actual temperature was measured by a chromel vs alumel thermocouple. These added points fell on the same straight line determined by the original calibration and serve as additional support for the general validity of the calibration method. Figure 9 shows a typical calibration curve (Pt resistor #5). Note that there are three points clustered at 0°C and four points at 25°C . These extra points were taken over a two week period and helped establish the stability and repeatability of the sensors. By taking the slope of this curve, the thermometer sensitivity was determined. For this particular resistor, the sensitivity was $2.26^\circ\text{C}/\Omega$ (or $0.443 \Omega/^\circ\text{C}$). In this resistance range, resistance changes of smaller than 0.1Ω could be detected using a four place Rubicon Model 1352 Wheatstone Bridge and a Leeds & Northrup Model 2430 A optical null detector. Therefore, temperature changes as small as 0.2°C could be detected. It is estimated that the overall temperature error - including instrumentation, leads, and interpolation - was $\pm 2.0^\circ\text{C}$. The thermometers varied from one to another in their sensitivity and repeatability. In general, all sensors

Fig. 9. Resistance vs temperature curve obtained in a typical calibration of the platinum thin-film temperature sensor.

repeated their calibration points before and after the sample was sputtered, and all were significantly sensitive to detect film temperature changes greater than 1.0°C . This sensitivity was more than adequate for the present experiments.

One problem noted on some of the sensors was a peeling and cracking of the SiO_2 protective layer. A similar phenomenon has been noted on SiO thin films.⁵⁴ This peeling is probably due to the thermal shocks suffered by the substrate, but its irregular occurrence prevented further investigation of the problem.

During film depositions, the sensor substrate was positioned in the middle of the substrate holder bottom plate and held in place by a stainless steel retainer and four stainless steel screws. As shown in Fig. 10 (A), this retainer was 5.1 cm (2 in.) in diameter and had 0.16 cm (1/16 in.) wide ledges which supported the substrate. On these ledges were mounted two phosphor bronze clip leads which contacted the Mo pads of the Pt resistance thermometer. The phosphor-bronze leads were electrically insulated from the retainer by a layer of Dow Corning "Silastic 732 RTV" adhesive/sealant [Fig. 10 (B)]. The ledges of the retainer served to shield the thermometer contacts from direct bombardment during sputtering. Teflon insulated copper wire leads were welded phosphor bronze clips. These leads were rf grounded by means of 500 pF capacitors and then connected to the Wheatstone bridge measuring circuit.

Tests were conducted to determine what effect target power level and applied bias would have on the surface temperature of a substrate thermally anchored with the Ga-In eutectic.

Fig. 10. Contact details for thin-film thermometer:

- (A) Special mask holder showing retainer ledge and placement of phosphor-bronze clip leads. Substrate with thermometer was placed face down over square opening so that molybdenum pads contacted the phosphor-bronze clips.
- (B) Detail showing how Silastic was used to insulate lead from mask holder.

Figure 11 shows the substrate temperature effect as a function of applied rf bias for a series of constant sputtering powers. The points were taken after the sputtering had proceeded for a few minutes and equilibrium had been reached. The data are for an initial ambient temperature of 18°C. As would be expected, the surface temperature rises both as power level is increased and as the bias applied to the substrate is increased. It is a general rule that 25% to 40% of the power applied to the target actually causes substrate heating through the mechanism of secondary electron collisions with the substrate.^{25,55} Because of this secondary electron heating effect, the substrate temperature would be expected to rise as power level is increased. As the applied bias is increased, more heating is caused by ion bombardment of the substrate.

The temperature rise due to power level with 0% bias can be accounted for theoretically by thermal conductivity considerations. Corning specifies the thermal conductivity of 7059 glass as between 2 cal/ms K and 4 cal/ms K. Taking 3 cal/ms K (0.0126W/cm K) as an average value, knowing the size of both target and substrate, and assuming that 32 1/2% of the applied power goes into heat at the substrate, one computes that the temperature difference across the 0.08 cm (1/32 in.) thick substrate should be $1.1^{\circ} \pm 33\%$ ($\pm 0.4^{\circ}\text{C}$) at 100 watts applied power and $2.2^{\circ} \pm 33\%$ ($\pm 0.7^{\circ}\text{C}$) at 200 watts. Similarly for the 0.635 cm (0.25 in.) thick stainless steel holder plate, with a thermal conductivity⁵⁶ of 0.15W/cm K, the temperature difference would be 0.8° at 100 watts and 1.6° at 200 watts. The predicted temperature difference between substrate face and cooling coil

Fig. 11. Substrate temperature rise vs substrate bias. Ambient temperature ($\Delta T = 0^{\circ}\text{C}$ on graph) was 18°C .

is then $1.90^{\circ} \pm 0.42^{\circ}$ for 100 watts applied power and $3.80^{\circ} \pm 0.70^{\circ}$ for 200 watts applied power and similarly for the other power levels. The measured values for these power levels at 0% bias are 2.00° and 4.40° respectively. The calculation does neglect probable temperature drops across the Ga-In interface between the substrate and the stainless steel holder. Inclusion of even a small temperature difference across this interface would easily put the measured temperature differences within the calculated limits.

Similarly, the temperature effects of changing bias can be accounted for in terms of the thermal conductivities of the substrate, interface and holder. Only now it is necessary at some of the higher bias levels to assume a 20° drop across the interface in order to explain the measured results. This interface contribution is about the same size as the drop across the stainless steel holder, and does indicate a thermally well anchored substrate.

The results of these tests show that the Ga-In eutectic is a very good material for thermally anchoring the substrates to their holder. It compares favorably to DeKhotinsky cement mentioned by Thornburg and Wayman⁵⁷ in evaporation applications. In addition one sees that at 200W and 15% applied bias, the total substrate temperature rise is less than 100° above the holder ambient temperature. So even during runs in which a sensor is not used, one can confidently assume that the substrate is at approximately the same temperature as the substrate holder (that is, at the coolant temperature). Finally, the curves of Fig. 11 permit one to

make a first order correction when trying to separate the combined effects of applied bias and temperature on the film composition.

Temperature measurements were made as a function of time during the deposition of the films. A typical result is shown in Fig. 12 for a 200W, 0% bias run of 30 minutes. When the shutter is initially opened, the substrate temperature almost instantaneously rises 2.5°C due to the secondary electron bombardment of the substrate. This rise is less than the 4.4°C rise shown in Fig. 11 for similar conditions, but the readings were taken with different sensors and are within acceptable experimental error. During the next 2 1/2 minutes the substrate temperature rises another 0.5°C , after which the temperature remains quite steady with only a small rise of 0.25°C in the last 10 minutes of the run. The implications here, are (as previously reported⁵⁷) that the substrate initially undergoes a temperature rise of short duration before it reaches equilibrium. It then maintains a steady temperature throughout the run. Thus one can assign a deposition temperature to a given sample with confidence that the film was at approximately that temperature for the complete deposition.

Fig. 12. Substrate temperature rise during a typical 30 minute sputtering run at 200 watts output power, no bias.

VI. RESULTS

The samples were compositionally analyzed for weight percent of the Te, As, and Ge constituents with an Applied Research Lab Model EMX electron microprobe. The microprobe readings were tabulated and converted to atomic percent of the constituents by a standard computer program "Magic IV."⁵⁸ The primary beam voltage was 7 keV which provided a sample current of approximately 20 nA. The L - α spectral line was used to detect the counts for all three constituents.

Several microprobe readings were taken within 100 μm of the center of each sample substrate. To prevent sample heating and the possibility of vaporizing the film's constituents, the sample was moved under the electron beam at the rate of 96 $\mu\text{m}/\text{minute}$ during the 40 second integration time (counting time) of each measurement. The composition of each film did not vary by more than a few tenths atomic percent as determined by these individual readings, and the arithmetic average of these separate measurements was used to specify the film's actual composition.

The microprobe was calibrated with bulk standards consisting of Te, As, and Ge pieces that came from the same lot of material that was used for the target. The mean depth of beam penetration into the film was 0.3 μm . Since all films were thicker than 1.0 μm , there was no problem with breakthrough to the substrate, and bulk standards were satisfactory calibration sources. The absolute accuracy of these analyses was ± 2 at%,⁵⁸ which includes instrumental errors, standardization errors, and small variations in beam locations on the film.

To place this possible error in perspective, it should be pointed out that the relative change between different compositions was precise to about ± 0.2 at%. So although one may be somewhat in error in reporting the exact composition of a sample, he can be much more certain of the relative compositions of any two or more different samples. And it is these relative changes which are important, for the interest lies more in how the composition varies with the different cosputtering, bias, and temperature effects, rather than in the exact composition achieved. Also, no attempt was made to determine the amount of possible argon inclusion in the films because no argon standard was available and because the microprobe had only three detectors which were used for the Te, As, and Ge respectively.

Initial data by the author⁵⁹ for the Te-As-Ge system is shown in Fig. 13(A). The solid points are for samples made at 20°C, and the open points are for samples made at -150°C. Figure 13(B) shows the complete Te-As-Ge ternary diagram. The dashed boundaries indicate the two bulk glass forming regions referred to in the introduction.⁹ The shaded section locates the position of the area which has been expanded to give Fig. 13(A). The main target has a $\text{Te}_{75}\text{As}_{25}$ composition. When Ge subtargets are added to this main target, the film composition should follow upward along the constant As/Te ratio line shown extending upward from the Te-As line to Ge in Figs. 13(A) and 13(B), provided that all of the Te and As which leave the target are incorporated into the film. The data points in Fig. 13(A) show that the film composition does not follow this line. Clearly, all of the Te from the target was not

Fig. 13. Initial compositions produced in the Te-As-Ge system.

- (A) Expanded view of shaded area in Fig. 13(B). The solid points were produced at 20°C substrate temperature and the open points were made at -150°C. Solid and dashed lines along data points denote compositions of the same nominal Ge concentration and have no physical meaning. Solid line at left edge indicates compositions which should be obtained if films reproduced the target composition.
- (B) Complete Te-As-Ge ternary system. Dashed boundaries indicate the bulk glass forming regions. The shaded area shows the region examined in this study. Solid line extending upward from Te-As border to Ge indicates film compositions that should be obtained for the target used.

being incorporated into the films.

From 20°C to -150°C Fig. 13(A) shows that the Te content increases, indicating that the Te is sticking better at lower temperatures, as might be expected. The effect of substrate bias at both temperatures is generally the same. There is some disorder at the lower bias levels, but the trend is clear that at the highest bias, a Te decrease occurs which has been attributed⁵⁹ to a preferential resputtering of the Te. A look at the Ge concentrations shows that, in general, the predictions made by the cosputtering equations of section 11 are accurate. The nominal Ge values predicted for this run were 4 1/2 at% Ge, 9 at% Ge, and 12 at% Ge. There are effects on the Ge concentration due to both temperature and bias, but overall, the actual Ge concentrations maintain their relative levels and also remain close to their predicted nominal values.

This initial data indicated the need for a more comprehensive look at the system as a function of bias and temperature. An almost limitless number of bias and temperature combinations were possible, and it was necessary to limit the actual conditions used. Since the general trend caused by bias was seen at both temperatures of Fig. 13(A), it was decided to make an extensive study of the bias effects at one temperature, namely 20°C, which was achieved by water cooling the substrate holder. Figure 14 shows the results of this study for four different Ge levels - no Ge (0 at% Ge), 2 at% Ge, 8 1/4 at% Ge, and 16 1/2 at% Ge. Here again, the trend of Te decrease at higher biases is seen.

Fig. 14. Film compositions produced during a study of bias effects. Substrate temperature for all films was 20°C.

The range of bias in this study went from 0% (grounded substrate) to 25%. Attempts to deposit films at higher biases up to 50% were only partially successful due to the greatly increased time required to produce a film 1.0 μm thick. Also at these higher biases, contamination of the main target occurred due to resputtering (sputter-etching) of material from the substrate cover plate and other fixtures. The removal of this contamination required an inordinately long pre-sputtering time before the next film could be deposited. So although it was possible to produce films at a substrate bias higher than 25%, it was impractical to do so, and the present data was limited to biases of 25% and lower.

It should also be mentioned that the biases indicated on Figs. 13 and 14 are nominal applied biases determined from the setting of the calibrated dial that was used to adjust the power splitting feature of the rf generator and tuning network. At 0% bias, the substrate was grounded with an external clip lead, and there was no potential between substrate and ground. As soon as the clip lead was removed, approximately 100V appeared between the substrate and ground, even though the power split was not applying any bias to the substrate. This was an induced bias due to the presence of the plasma, and so even at very low nominal biases like 2 1/2% or 5%, there was approximately 100V on the substrate. This induced bias in no way invalidates the results of the investigation. It merely indicates that with this equipment, it is not possible to produce films that have an actual substrate voltage less than 100V, except for the zero volt condition of the grounded substrate.

A study of the substrate temperature as it affects film composition was also done, in this case at a single bias of 0% (grounded substrate). Zero bias was chosen for its convenience and its reproducibility. The control of the substrate temperature was done manually. This control was straightforward when LN_2 or water was used as the coolant; but when cold N_2 gas was being circulated or when the heater was on, conditions had to be continuously monitored to maintain a constant substrate temperature. An extensive study of temperature effects at many bias levels would have been difficult to achieve because exact reproducibility of the temperature was not possible. In addition, the heater inside the substrate holder would have required special feedthroughs and connections⁶⁰ in order to allow the application of bias when the heater was being used.

The study of temperature effects at only one bias (or the study of bias effects at one temperature) is not a serious limitation, because definite trends can be seen at the conditions examined. It is assumed that the compositional changes due to temperature at 0% bias would exhibit the same general trends at a different bias, as evidenced by the initial data of Fig. 13(A).

The specific compositions obtained as a function of temperature are shown on Fig. 15. A very interesting result seen in Fig. 15 is that at both the lowest temperatures and the highest temperatures, the atomic percent of arsenic decreases, which means the Te content increases. It had previously been reported by the author⁵⁹ that Te content decreases up to about 70°C in the Te-As system. In the present Te-As-Ge system,

Fig. 15. Film compositions obtained as a function of substrate temperature. Bias for all films was 0% (grounded substrate).

the T_e decreases until just above 20°C , and then begins to increase. This reversal will be discussed in the next section.

One additional fact about Fig. 15 is that the lowest temperature (-150°C) occurred when LN_2 was being circulated through the cooling coil of the substrate holder. The substrate temperature did not reach the -196°C temperature of LN_2 because the LN_2 itself was in dual phase with its gas and so the coolant itself was not at -196°C . There were also heat leaks from the ambient and heat input due to the sputtering, so the lowest temperature used in this study was -150°C .

VII. DISCUSSION

A. Initial Te Shift

One of the things obvious from Figs. 13-15 is the difference between target composition and film composition. This is most clearly evident from the 0 at% Ge, 0% bias point on Fig. 14 where a film of $\text{Te}_{68}\text{As}_{32}$ results from the $\text{Te}_{75}\text{As}_{25}$ target. Over and above any effects due to bias or temperature, the Te-As and Te-As-Ge systems exhibit a significant Te deficiency in the film composition. This Te loss is probably best explained as the result of a poor sticking coefficient for Te. The Te atoms do not stick to the substrate as well as the As atoms or the Ge atoms. In fact, if at 20°C one assumes that all the As atoms stick (sticking coefficient = 1.00), then a Te sticking coefficient of 0.61 would provide the film compositions actually obtained. The Te which does not adhere is reflected back into the plasma where it undergoes random collisions. At a $20\text{ }\mu\text{m}$ sputtering pressure, the mean free path between collisions is approximately 1 cm (0.4 in.). Some of the Te eventually returns to the substrate, but much of it is lost from the plasma and ends up on the fixtures due to the fact that the walls and the bell jar are only 2 or 3 cm (1.0 in.) from the sputtering target. A film deposition on the bell jar was observed during the sputtering runs. The poor sticking coefficient of Te, with the resultant loss of Te, accounts for the initial shift between film composition and target composition. It is probable that in a different sputtering system having different fixtures this initial loss of Te would be quantitatively

different. And if all the Te could be constrained to remain in the plasma, it should eventually deposit on the film and one should get films with the same composition as the target. Again it is emphasized that this initial shift is independent of bias effects or temperature effects. Bias and substrate temperature will cause additional changes in the film composition.

B. Cosputtering

The effects due to cosputtering are quite straightforward as is evidenced by Figs. 13-15; and the at% Ge values conform well to the predictions made by using Eqs. (2), (3), and (4) of section II. Figure 16 shows the at% Ge content of the films as a function of percent power split and also as a function of actual bias voltage. As mentioned previously, as soon as the substrate was disconnected from ground (0% bias case), an induced voltage of about 100V appeared on the substrate, and so a number of points on Fig. 16(B) are grouped at this 100V level of bias voltage. The solid lines in Fig. 16 represent the calculated values for Ge. The Ge makes a predictable contribution to the film content, as would be expected. One also sees a slight dip in the Ge concentration at the lower bias levels, and then a rise as bias is increased. These effects are due to the influence of bias and will be discussed along with the bias effects.

Figure 17 shows the Ge concentration at the various substrate temperatures examined. The solid lines are the calculated Ge levels, and again it is seen that predictable Ge concentrations are obtained. Generally, the Ge concentration is constant with respect to temperature,

Fig. 16. Atomic % Ge as a function of bias level. Solid lines denote predicted values for the at% Ge.

(A) Compositions as a function of the percent bias as determined by the power split control.

(B) The same compositions as in Fig. 16(A) as a function of the substrate bias voltage.

Fig. 17. Atomic % Ge as a function of the substrate temperature. Solid lines denote predicted values for at% Ge.

although there is evidence of a slight increase in Ge content at the lowest temperature, probably due to a somewhat enhanced sticking coefficient for Ge at this low temperature.

Table I compares the predicted and the measured values for the amount of Ge incorporated in the samples prepared at different biases and temperatures. Also shown is the actual difference (in at%) between the predicted Ge content and the measured Ge content. This difference was used to compute the % error shown in the last column. The overall rms percent error for the 2 at% Ge level is 32.5%, for the 8 1/4 at% Ge level it is 10.0%, and for the 16 1/2 at% Ge level it is 5.9%. As indicated by these overall rms percent errors, the cosputtering calculations are more accurate at the higher Ge levels. This fact most likely is attributable to the electron microprobe measurements, since for the 2 at% Ge level, an offset of 0.5 at% would produce a greater deviation than the same 0.5 at% offset at the 16 1/2 at% Ge level. In addition, the cosputtering calculations are inherently more accurate than the % rms error indicates because much of the Ge deviation comes at the higher biases where one observes not really a cosputtering effect but rather a bias effect. Realizing that the cosputtering predictions are probably more accurate than the % rms error indicates, one still finds that the accuracy of the cosputtering equations for the present case is comparable to the reported 25% rms accuracy for the dilute constituents of a multi-component film²² (which includes the 2 at% Ge level) and the 10% rms accuracy otherwise reported for the cosputtering equations.¹⁹

Table 1. Predicted and measured composition of cosputtered Ge.

Sputtering Parameters		Composition			
Bias	Temperature	Predicted (at% Ge)	Actual (at% Ge)	Difference in at%	% Error
0%	20°C	2.0	2.1	+0.1	5.0
		8.3	8.2	-0.1	1.2
		16.5	17.7	+1.2	7.3
2 1/2%	20°C	2.0	1.7	-0.3	15.0
		8.3	7.8	-0.5	6.0
		16.5	16.2	-0.3	1.8
5%	20°C	2.0	1.8	-0.2	10.0
		8.3	7.3	-1.0	12.0
		16.5	15.9	-0.6	3.6
7 1/2%	20°C	2.0	1.8	-0.2	10.0
		8.3	6.9	-1.4	16.7
		16.5	15.6	-0.9	5.5
10%	20°C	2.0	2.1	+0.1	5.0
		8.3	7.8	-0.5	6.0
		16.5	15.9	-0.6	3.6
15%	20°C	2.0	2.6	+0.6	30.0
		8.3	8.6	+0.3	3.6
		16.5	16.4	-0.1	0.6
16 1/4%	20°C	2.0	2.4	+0.4	20.0
		8.3	8.0	-0.3	3.6
		16.5	15.8	-0.7	4.2
17 1/2%	20°C	2.0	2.4	+0.4	20.0
		8.3	8.7	+0.4	4.8
		16.5	16.0	+0.5	3.0
18 3/4%	20°C	2.0	2.9	+0.9	45.0
		8.3	8.3	0.0	0.0
		16.5	16.0	-0.5	3.0
20%	20°C	2.0	3.0	+1.0	50.0
		8.3	9.1	+0.8	9.6
		16.5	16.8	+0.3	1.8

Table 1. (continued)

<u>Sputtering Parameters</u>		<u>Composition</u>			
Bias	Temperature	Predicted (at% Ge)	Actual (at% Ge)	Difference in at%	% Error
22 1/2%	20°C	2.0	3.2	+1.2	60.0
		8.3	9.5	+1.2	14.5
		16.5	-	-	-
25%	20°C	2.0	3.6	+1.6	80.0
		8.3	10.2	+1.9	22.9
		16.5	18.1	+1.6	9.7
0%	-150°C	2.0	2.7	+0.7	35.0
		8.3	9.8	+1.5	18.1
		16.5	18.3	+1.8	10.9
0%	-70°C	2.0	1.9	-0.1	5.0
		8.3	8.6	+0.3	3.6
		16.5	18.2	+1.7	10.3
0%	+20°C	2.0	2.1	+0.1	5.0
		8.3	8.2	-0.1	1.2
		16.5	17.7	+1.2	7.3
0%	+40°C	2.0	2.0	0.0	0.0
		8.3	8.3	0.0	0.0
		16.5	16.4	-0.1	6.1
0%	+60°C	2.0	2.0	0.0	0.0
		8.3	8.3	0.0	0.0
		16.5	17.2	+0.7	4.2
0%	+90°C	2.0	1.9	-0.1	5.0
		8.3	8.3	0.0	0.0
		16.5	17.9	+1.4	8.5

It is seen that the technique of cosputtering incorporates predictable amounts of the cosputtered material in the film produced. Using Ge as the cosputtered element, it is found that the Ge level in the films is somewhat affected by the substrate bias and is pretty much independent of the substrate temperature.

C. Temperature Effects

Figure 18(A) shows the at% Te composition for the Te-As films as a function of substrate temperature. Since the Ge levels were relatively constant as a function of temperature (Fig. 17), the As levels are not shown here since they compose the rest of the film content and their shape is roughly the inverse of the Te curve. There is some scatter in the data, but allowing a ± 1.0 at% Te error bar, the data can be readily fit to two straight lines with different slopes in the two temperature regions of -150°C to $+20^{\circ}\text{C}$ and $+20^{\circ}\text{C}$ to $+90^{\circ}\text{C}$. It should be noted that if the low temperature line were extended off the graph, it would intercept the 75 at% level at approximately -273°C (0 K). This fact lends some additional validity to the line drawn for these low temperature points, because one would expect that at 0 K all the material sputtered from the target would stick to the substrate and one should obtain films having the target composition.

The general increase in at% Te below 20°C is attributable to the increased sticking coefficient of Te at lower temperatures. If one assumes that almost all of the As sticks over this temperature range from -150°C to 20°C and that more Te sticks at the colder temperatures,

Fig. 18. Effects of substrate temperature on Te:
(A) Atomic % Te as a function of substrate temperature.
(B) Sticking coefficient of Te as a function of substrate temperature.

the film will show a higher at% for Te. There will be a corresponding decrease in the at% of As.

When one is below 20°C, a sputtered atom striking the substrate and sticking will most probably remain exactly where it hit. Due to the low temperatures, there is not enough energy for the atom to move about and form the most favorable bonds. So the increase in Te at low temperatures is due strictly to the fact that more of the Te sputtered from the target actually sticks to the substrate.

Above 20°C, there is more energy available to the atoms on the substrate, and they can adjust themselves a bit after striking to form more favorable (higher energy) bonds. It is suspected that this effect is occurring for these samples and that the Te is able to form some stronger bonds and thus stick better to the film at higher temperature. The temperature at which the bonds can start to rearrange and form energy-favorable configurations is called the glass transition temperature. This glass forming temperature is about 82°C for a $\text{Te}_{75}\text{As}_{25}$ composition.⁶¹ There is no specific glass transition temperature data for the composition studied here. It is known, however, that the samples in this study are on the edge of the glass forming region, and as such, the glass transition temperature will drop.¹⁷ So it is very reasonable to believe that the increased Te in the films produced above 20°C is due to the fact that again Te has a better chance to stick to the growing film, this time because it can form stronger bonds with the other constituents. And the line above 20°C intercepts the 75 at% Te level at about 130°C. This is perhaps coincidental, but the glass crystallization temperature for

$\text{Te}_{75}\text{As}_{25}$ has been reported⁶¹ as 132°C . Above the crystallization temperature, one would no longer have amorphous films, since crystal structure would occur. And it is likely that in crystalline form, all the Te could find satisfying bonds and thus all the Te would again stick to the growing film.

The results shown in Fig. 18(A) imply that one can get the same film compositions over the temperature range 20°C to 90°C as over the temperature range -150°C to 20°C . Since it is easier to use the substrate heater than to use cooling gases, it appears that the way to obtain various compositions is to use the 20°C to 90°C range. But this might not be true for different amorphous systems that have higher glass formation temperatures.

Assuming that the solid lines in Fig. 18(A) do represent the actual at% Te in the films, one can determine the sticking coefficient for Te at any and all given temperatures. For example, at 20°C , the film composition is 64.6 at% Te and 35.4 at% As. The As/Te ratio is equal to 0.55. Assuming that all the As atoms stick for the temperature range considered, one knows that for every 25 As atoms in the film, there must be 45.5 Te atoms. But for every 25 As atoms that leave the target, 75 Te atoms leave. Thus the sticking coefficient for Te at 20°C is $45.5/75 = 0.61$. Similarly, the Te sticking coefficients at other temperatures can be computed, and a plot of the Te sticking coefficient as a function of temperature is shown in Fig. 18(B).

The Te sticking coefficient is linear in both regions and has a slope of $-1.12 \times 10^{-3}/^{\circ}\text{C}$ below 20°C and a slope of $3.25 \times 10^{-3}/^{\circ}\text{C}$.

above 20°C. The preceding considerations concern only the Te-As system, but one can now use the Te sticking coefficients to predict the amount of Te that should occur in the Te-As-Ge cosputtered films. Figure 19 shows the amounts of Te in the films as predicted from the sticking coefficient and the actual at% Te measured in the films as a function of substrate temperature. One sees that at all three Ge levels, the actual at% Te is higher than that which the Te sticking coefficient predicts. There exists another mechanism which enhances the sticking of Te. The explanation for this Te enhancement is found in the fact that the presence of Ge provides a new bonding partner for Te. The sticking coefficient predictions did not consider the presence of Ge, but only predicted the amount of Te that would stick for this given physical sputtering geometry in the Te-As system. The addition of Ge provides new possibilities to hold on to some more Te.

The effect of Ge is relatively greater at the 2 at% Ge level where the Te increase has a mean value of 4.3 at% Te, compared to a mean increase of 2.0 at% Te at the 8 1/4 at% Ge level and the mean increase 3.4 at% Te at 16 1/2 at% Ge.

Table 2 shows the relative order of the 6 possible bonds in the in the Te-As-Ge system. The atoms form covalent bonds, with Ge having four bonds, As three, and Te two. The Te-As samples in this study are all on the Te rich side of the stoichiometric composition As_2Te_3 ($\text{Te}_{60}\text{As}_{40}$). The samples will contain numerous weak Te-Te bonds. Adding a small amount of Ge enables the relatively stronger Ge-Te bonds to form, and this bonding ties down more of the Te that reaches the substrate.

Fig. 19. Atomic % Te as a function of substrate temperature showing the effects of Ge bonding. Solid points joined by solid line have been calculated from Te sticking coefficients. Crosses indicate measured film compositions.

Table 2. Bond energies in Te-As-Ge system^a

<u>Bond</u>	<u>Energy (KJ/mole)</u>
Ge-Ge	188
Ge-As	187
As-As	180
Ge-Te	156
As-Te	152
Te-Te	123

^aValues for bond energies supplied by A. J. Bevelo, Ames Laboratory - USAEC.

And so the at% Te increases, with a resultant decrease in the at% As. Now if more Ge is added, say $8 \frac{1}{4}$ at%, in addition to tying down Te, there will also be a greater probability of forming the strong Ge-As bonds, in which case As will also be bonded better. One could expect that now some more As will also be incorporated in the film, thereby proportionately reducing the increase in at% Te. It seems that the bonding effect saturates at about the $8 \frac{1}{4}$ at% Ge level, because a doubling of the Ge concentration to $16 \frac{1}{2}$ at% Ge about doubles the at% Te content. By considering the bonds available to the Te, As, and Ge, one can understand the physical reason for the Ge enhancement of the Te content of the films.

D. Bias Effects

The predominant effect caused by substrate bias is a decrease in Te composition of the film due to preferential resputtering of the Te. Figure 20 illustrates how the Te content decreases as bias increases. As predicted by Winters and co-workers,²⁰ Te should preferentially resputter because it has the largest size of the three film constituents (atomic radii: Te = 1.60 Å, As = 1.25 Å, Ge = 1.37 Å).⁶² The larger size of Te means that Te presents a larger cross-section to incoming particles and therefore has a greater chance of being hit and being resputtered.

There is again some scatter in the data, but if one takes a ± 1 at% Te error bar (not illustrated), the points can be fit to the straight lines shown. All these curves have the same slope of -0.025 at% Te/V. Since no information has been reported concerning the sputtering threshold or the sputtering yield of Te, this slope can unfortunately not be related to any physical quantity. The slope does give one the experimental means to obtain a desired Te composition in a film because the application of a certain bias will yield films deficient in Te by a predictable amount.

One would like to examine Eq. (5) of section II to see if it has any validity for the present system. It should be pointed out that in Eq. (5), V_b is the effective bias potential, and

$$V_b = V_a - V_p \quad (6)$$

where V_a is the applied bias and V_p is the plasma potential.

Fig. 20. Atomic % Te as a function of substrate bias showing effect of Te preferentially resputtering.

Equation (5) does predict that the film composition will be the same as the target composition when $V_b = 0$, that is, when the applied potential V_a equals the plasma potential V_p . In the Te-As and Te-As-Ge systems, equivalent film and target compositions are never achieved due to the initial loss of Te.

A correction can be made for the initial departure of Te from the film composition.

Since Eq. (5) uses a ratio of two film constituents, the data from some of the bias runs was plotted in Fig. 21 as As/Te ratio vs bias voltage. The crosses represent the actual As/Te ratios, and the error bars were obtained by allowing a ± 1.0 at% error in each constituent. It should be noted that the points in Fig. 21 are for Te-As only (no Ge). The measured points and known voltages were used in Eq. (5) to obtain a best fit value for the parameter K . Published reports²⁹ indicate K is of the order of 1.0, and for this data, a best fit value for K was $K = 0.33$. Using this K value, a predicted composition was calculated for As/Te and is shown as the solid line in Fig. 21. This theoretical curve for the As/Te ratio is a parabola, at least up to the 200V bias level.

One is at a loss to explain the two anomalous points of Fig. 21. They are real points, and it would be pushing the data to try to extend their error bars to include the predicted values. A possible explanation for the anomaly involves the sputtering threshold voltage for Te. As mentioned before, the value of the Te threshold voltage is not known, but if it were on the order of 125V (a not unreasonable value since

Fig. 21. As/Te ratio vs bias voltage. Solid line is calculated value for As/Te ratio using Eq. (5).

some known thresholds include Co at 120V²⁹) it could account for these two points. Below 125V bias, the Te is not resputtering, but maybe a little As is lost, so the As/Te ratio drops. Once above 125V or so, the preferential Te resputtering occurs.

Based on the limited number of data points studied, it would be hard to draw a definite conclusion regarding Eq. (5). It does predict fairly well the As/Te ratio at higher bias voltages, but it fails to account for possible threshold voltages. A more complicated equation from which Eq. (5) is derived²⁹ does include threshold voltage as a parameter, but it also requires knowledge of sputtering yields plus other parameters that are not known for the Te-As system. A basic assumption of Eq. (5) is that the accumulation rate of the individual film constituents can be treated independently. Since it has been demonstrated that Ge concentrations have an enhancing effect on Te, the equation should not be considered to apply to the Te-As-Ge system. But in lieu of Eq. (5), it is seen from Fig. 20 that a direct relationship does exist between the Te content and the bias.

VIII. SUMMARY

This thesis has demonstrated that three separate techniques involving cosputtering, control of film temperatures, and control of film bias can be used in combination to produce films with a wide range of compositions in the Te-As-Ge system from a single main sputtering target.

There was an initial shift in composition between the Te-As main target and the film compositions due to a loss of Te from the sputtering plasma. This loss occurred because Te had a relatively lower sticking coefficient than As. The use of cosputtering introduced predictable amounts of Ge into the films. The Ge content of the films was essentially independent of substrate temperature and exhibited a gradual increase as bias was increased. The substrate temperature had an effect on the As/Te ratio through its influence on the sticking coefficient of Te. The temperature range examined could be divided into two parts - -150°C to 20°C and 20°C to 90°C . The same changes in As/Te composition were observed for both ranges, with the implication that either range (whichever is most convenient) could be chosen to produce films in this system. Application of an rf bias to the substrate also induced changes in the As/Te due to the preferential resputtering of Te. This observed preferential resputtering of Te conforms to theoretical predictions. An attempt to predict the alteration in Te-As film compositions due to an applied bias by using a previously reported equation was partially successful though the equation failed to account for a

possible threshold effect. A more complex equation required some basic sputtering parameters for Te and As which are not presently known. However, a simple linear relationship between Te content and bias was observed in Te-As-Ge films.

In the course of this research, a thin film sputtering facility has been constructed and operated. Also developed during this research was a platinum thin-film temperature sensor that was used to record the substrate temperature during film deposition.

The implications of this research are that the proper choice of sputtering techniques and the careful control of sputtering parameters will enable one to prepare many compositionally different samples of binary, ternary and higher order systems in an economical and convenient manner.

There are some things that could be done to improve the equipment and to complete the investigation of this system. The application of a magnetic field would be very helpful for confining the plasma and increasing the sputtering efficiency. It would be interesting to apply a confining magnetic field and see if it would prevent the initial loss of Te which was experienced in this work.

It would also be desirable to design an automatic controller for the substrate holder temperature, especially if one intends to do extensive sputtering at temperatures other than water or LN_2 . This holder would have to incorporate some special shielding and isolation techniques so that bias could concurrently be applied to the substrate.

To get a complete picture of how all the sputtering parameters affect film composition, a series of runs could be made in which sputtering pressure and sputtering power were varied, while holding temperature and bias constant.

It would also be worthwhile to sputter a main target with a composition different from the $\text{Te}_{75}\text{As}_{25}$ presently used in order to confirm that the same effects do occur. And finally, a series of runs with different at% Ge (say 3 at%, 6 at%, and 9 at%) could be made to see where the Ge bonding saturation occurs (refer to Fig. 19 and related discussion).

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