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PREPARATION AND CHARACTERIZATION OF HYDROGENATED AMORPHOUS
SILICON THIN FILMS AND THIN FILM SOLAR CELLS PRODUCED BY ION
PLATING TECHNIQUES

Final Report for Period January 1, 1979—May 31, 1980

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May 1980

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ABSTRACT

Ion plating techniques for the preparation of hydrogenated amorphous silicon thin films have been successfully developed. The technique involves essentially the evaporation of elemental silicon through a d.c. produced hydrogen plasma. In this way hydrogen has been successfully incorporated into amorphous silicon films in concentrations as high as 30 atomic percent. Infrared spectroscopy indicates the usual SiH_x stretching mode at approximately 2000 cm^{-1} . Further evidence for the bonding of hydrogen was obtained from ESR measurement of hydrogenated and unhydrogenated samples. The measured unpaired spin density was a factor of 25 less in the hydrogenated sample. The optical absorption edges of the hydrogenated films fell in the usual range between 1.7 and 1.9 eV. Electrical conductivity measurements indicated a substantial reduction in the density of defect states in the gap as expected. It was also shown that hydrogenated amorphous silicon prepared by ion-plating could be doped by co-evaporation of the dopant element during film deposition. Both co-evaporated phosphorous and co-evaporated bismuth have been found to substantially increase the dark conductivity of a-Si:H while shifting the Fermi level towards the conduction band edge. An x-ray method for estimating the density and hydrogen content of a-Si:H has been developed. Although the densities of these films have been measured by flotation methods and hydrogen contents determined by infrared absorption and resonant nuclear reaction techniques, the x-ray method discussed in this paper is inherently simple and completely

nondestructive. By utilizing the absorption in the film of the fluorescent radiation from the substrate, the actual mass of silicon present per unit area can be determined directly. Because of its relatively long wavelength fluorescent radiation, titanium is the preferred refractory metal substrate material for this procedure. This mass per unit area value can be used, together with the measured thickness, to estimate closely the film density and the concomitant film hydrogen content. Measurement of the mass of silicon present may also have direct utility in assessing the kinetics of film preparation methods. The measurement of strain in a-Si:H thin films is discussed also.

I. INTRODUCTION

Ion plating is a deposition process in which evaporation of a metal or semiconductor into a plasma glow discharge about a negatively biased substrate is used to affect both the character and the surface bonding of the resulting thin film deposit. Ion plating has also been carried out by direct ion beam methods but can still be distinguished from ion implantation by the use of the low ion energies typical of glow discharges. The energy level of the evaporated metal or semiconductor is increased through their interaction with the glow discharge. It is the increased energy state of the depositing material that affects both the nature and adherence of the deposited thin films. The term ion plating was itself introduced in 1964 by Mattox (Mattox, 1964)*. To date, the method of ion plating has been used primarily for the coating of substrate materials, including non-conductors such as plastics, with metals. This is so because an immediately recognized advantage of this method was the drastically improved adhesion of ion plated films versus vacuum deposited films (Davis, 1963). This increase in adhesion is due to the controllable arrival energy of the incident metal vapor flux. Both the glow discharge voltage and evaporation rate can be separately controlled (Aisenberg and Chabot 1973).

Recently, the related method of ionized cluster beam deposition has been used to produce epitaxial semiconductor films of silicon on substrates of single crystal silicon amorphous carbon, and cleaved NaCl, which has a lattice parameter within 3% of that of silicon (Takagi et al., 1978 , Takagi et al., 1976). In these experiments the ionizing vapor was composed of thermionically generated electrons rather than the more usual use of evaporation into a glow discharge.

*All references are listed in alphabetical order in Section VIII.

Moderate voltages and large cluster sizes have been found to increase crystallinity (Takagi, 1976). Conversely, higher voltages and small cluster sizes decreased crystallinity (Mattox, 1973). It is to be expected that, with low substrate temperatures, high glow voltages and relatively small cluster sizes, that amorphous silicon films can be readily produced since, in normal glow discharge methods amorphous silicon films can be made on substrates whose temperatures are over 500°K (Loveland, et al., 1973). To date, however, only one parenthetical report involving amorphous silicon films and ion plating appears to have been presented in the literature (Itoh, 1977). Itoh, however, devoted most of his experimental effort to producing single crystal epitaxial silicon films on the (111) and (110) planes of single crystal silicon substrates.

Work by Carlson (Carlson, 1977) and others on glow discharge decomposition of silane and work by the Harvard group (Paul et al., 1976), (Moustakas, et al., 1977) on reactive sputtering have shown that the crucial factor in achieving reasonable semiconducting properties in amorphous silicon appears to be the incorporation of hydrogen within the film to fill the dangling bonds occurring as a result of incomplete bonding in the disordered amorphous matrix. This reduces the low temperature conductivity by eliminating most of the defect states within the bandgap which leads to hopping conduction. Additionally, there is a reduction in the magnitude of the electron spin resonance, which correlates with the number of electrons on void surfaces (Lewis, 1976). Brodsky has characterized the hydrogenation by IR and Raman spectra (Brodsky et al., 1977). In the glow discharge process, hydrogenation is accomplished as a byproduct of silicon deposition from an ionized plasma of silane. For many years the properties of silicon films from glow discharges were recognized to be anamously superior to other amorphous silicon films, though the theory of the incorporation and influence of hydrogen was discounted (Le Comber, et al., 1973).

Accepting hydrogenation as the critical factor in producing films suitable for solar cell applications, reactive ion plating techniques offer many advantages and new experimentally variable deposition conditions over reactive sputtering and glow discharge decomposition and concomitantly therefore many new possibilities for improving cell efficiencies.

In the glow discharge process, hydrogenation has been accomplished primarily through the hydrogen produced by the decomposition of the silane (SiH_4). In reactive sputtering using hydrogen, however, all incorporated hydrogen must, of course, come from the hydrogen plasma itself. For ion plating, control of the degree of hydrogen incorporation is possible through the regulation of the partial pressure of hydrogen, the partial pressure of silane, the accelerating potentials in the system, and the cluster size. If silane is used, of course, then both deposition from the glow as well as cluster deposition of evaporated silicon will simultaneously occur. Likewise, some degree of control of cluster size is available by regulation of these same experimental parameters, as well as by the evaporation of silicon into a small chamber to create a plasma of silicon which, when released, will supercool by adiabatic expansion and cause the atoms to agglomerate and form clusters typically containing 100 - 200 atoms (Takagi, et al., 1978). This additionally affords another degree of control of the extent of hydrogenation by virtue of control of the specific surface area of the atoms. Since the cluster size also affects the charge-mass ratio, electrostatic and magnetic fields may be used to selectively enhance deposition of large- or small-mass ionized vapor clusters. The anticipated deposition rates for ion plating are somewhat lower than for evaporation alone because of gas scattering and self sputtering of the deposited film, but still are far higher than for sputtering ($3.5 \text{ \AA}/\text{sec}$) or glow discharge decomposition ($10 \text{ \AA}/\text{sec}$). An unsigned article in a plastics trade magazine reports ion plating rates of 1 mil/min being achieved for aluminum at a

distance of 10 inches (Anon, 1976). While this figure should be regarded as an upper limit, it does indicate the potential of the process for eventual rapid production of solar cells. The uniquely high adhesive properties of ion plated films accounts for their main application in coating difficult materials such as plastics, and this characteristic would enable them to adhere to a wide variety of inexpensive substrates such as metallized glass, thin plastic metallized films, and various metals. For best results in the thermally cycling environment of a solar cell, some attention must be paid to matching the coefficients of linear thermal expansion, although film flaking is not likely if adhesion typical of ion plated metal films is achieved.

Two options for doping of ion plated films are apparent. The dopant could be injected into the system as a gas (e.g., phosphine, (PH_3) or diborane (B_2H_6)) with the hydrogen and be incorporated into the film in much the same manner as practiced in reactive sputtering (Paul, et al., 1976). Alternatively, aluminum, gallium, or indium could be co-evaporated with the silicon to form p-type material or arsenic or antimony could be used for n-type doping.

If the doping is accomplished by co-evaporation of the dopant species, an attractive benefit is the speed with which doping types can be changed while the silicon evaporates continuously. Theoretically, the fabrication of an entire cell from sputter cleaning of the substrate to surface contacting and antireflection coating could be accomplished in a single system pump down at a respectable rate because of the speed and variety of depositions possible in an ion plating system. This factor would constitute an especially significant advantage in the eventual commercial production of amorphous thin film solar cells.

As we will now show in the following section, ion-plating both with and without magnetic fields has indeed been used successfully to produce hydrogenated amorphous silicon thin films with hydrogen contents of up to 30 atomic percent. In addition,

co-evaporation has been used to dope these films with both phosphorous and bismuth. A thorough program of film evaluation has been carried out to characterize these films in detail and this work is presented in Section IV.

II. FILM PREPARATION

During the course of this program two independent techniques have been used to prepare hydrogenated amorphous silicon. These techniques are glow discharge decomposition of silane and ion-plating of amorphous silicon by evaporation through a hydrogen plasma.

A. Glow Discharge Decomposition of Silane.

The glow discharge system was modified to include an electromagnet that can be used to produce magnetic fields perpendicular to the substrate surface ranging from 0 to .12 tesla (1200 gauss). This system was used to produce some seventy a-Si thin films using various magnetic field intensities to constrict and enhance the glow. The results of these experiments, discussed in Section III, indicate that magnetic containment can be used to more than double the deposition rate at a given power input to the glow.

B. Ion Plating.

Ion plated films were produced using a modified Tagaki ion cluster apparatus. In this system hydrogenated amorphous silicon films were prepared by evaporating silicon through a hydrogen gas plasma.

The experimental apparatus used to produce these films is shown schematically in Figure 1. It consists of a 750 kHz RF generator which feeds power through a 12:1 RF step-down transformer, to a power coil located inside the vacuum chamber. The use of an RF transformer is necessary in order to avoid the arcing which would otherwise occur when using a 750 kHz RF source at low gas pressures. The silicon

Figure 1. Ion Plating Apparatus.

to be evaporated is contained by a boron nitride crucible resting within a graphite susceptor that is in turn thermally insulated using zirconium oxide felt. As can be seen from Figure 1, the glow is produced by an annular cathode which is axially arranged below the grounded substrate holder. This holder is in turn fitted with heating elements for substrate temperature control. The substrate temperature was approximately 300°C. Hydrogen pressures were directly measured using a liquid nitrogen baffled McLeod gauge, and was typically, 100 microns. Before backfilling with electronic grade hydrogen, this system was evacuated to 1×10^{-6} torr by a liquid nitrogen - baffled oil diffusion pump.

The experimental apparatus was later modified by replacing the boron nitrate (BN) crucible with a beryllium oxide (BeO) crucible. BeO has advantages in that it has excellent high temperature thermal conductivity and avoids the dangers of accidental doping of the films with boron, a p-type dopant in amorphous silicon. A resistively heated tungsten boat was also substituted for the r.f. heated graphite susceptor.

III. MAGNETIC FIELD CONFINEMENT EFFECTS

Experimental use of magnetic fields to compress and constrict plasmas is, of course, well known (Bishop 1958; Rose and Clark, 1961). Magnetic fields have also been used to enhance the rate of sputtering in the glow discharge etching of metals (Newkirk and Martin, 1958; Padden and Cain, 1954; Fisher and Weber, 1952). There does not appear, however, to have been any previous systematic attempts at enhancing the deposition rate of amorphous silicon thin films during preparation by the glow-discharge decomposition of silane.

In this segment of our work we have utilized a C-shaped magnet to produce fields of up to 0.12 tesla (1200 gauss) normal to both the deposition substrate and the cathode plate. This cathode plate is austenitic stainless steel since it is known that the sputtering rate of such steels is low (Southern, et al., 1969).

Figure 2 shows the dependence of deposition rate on applied magnetic field. In these experiments the feed-gas composition was 10% silane by volume in argon and the gas pressure in the chamber was kept in the range of 0.35 - 1.0 torr as directly measured with a mercury McLeod gauge. The data at essentially zero magnetic field were obtained with the magnet core still in place, but with the residual magnetism of the core removed. As expected, since the only effect of field polarity is on the direction of spiralling of the charged ions, an experiment carried out at 0.20 tesla (2000 gauss) with reversed field showed no difference.

As expected, the application of the field acts to confine the plasma between the poles of the magnet, hence confine the deposition produced by this glow discharge to the substrate. The magnetic induction B produces an effective pressure $B^2/2\mu_0$ which serves to compress the discharge between the magnet pole faces (Uman, 1964).

Figure 2. Deposition rate as a function of magnetic field intensity.

The kinetic pressure rises with particle density until equilibrium is achieved. As seen from Figure 2, the deposition rate can indeed be more than doubled by the application of the field.

The field confinement effect, of course, acts to increase plasma conductivity, hence glow discharge current (at constant voltage). In these experiments the discharge current was held constant at 10 ma/cm^2 by varying the voltage from about 1200 volts at zero field to 750 volts at 0.12 tesla.

IV. FILM CHARACTERIZATION

A. Infrared Spectroscopy.

Typical infrared absorption spectra obtained from glow discharged produced a-Si thin films showed two absorption peaks. That peak located at a wavenumber of $\sim 2090 \text{ cm}^{-1}$ is due to a stretching mode associated with SiH_x , while the peak at a wavenumber of $\sim 2000 \text{ cm}^{-1}$ is associated with the SiH stretching mode (Tsai, et. al., 1977). The spectrum shown in Figure 4 was obtained using the same ratio of silane to argon, voltage and glow current, but at a pressure of ~ 1.00 torr. Note that the only absorption peak observed is at $\sim 2090 \text{ cm}^{-1}$ which corresponds to SiH_2 stretching. This result is consistent with observations made by Brodsky (1977B).

Infrared absorption spectra were also obtained for the ion-plated films. A spectrum from a film prepared by evaporation through a hydrogen plasma at a nominal hydrogen pressure of 100μ . This film which was prepared during the early part of the program showed the typical Si- H_x stretching doublet. It is shifted slightly to a higher frequency than usually observed, this is attributed to contamination that occurred in our vacuum apparatus during the early stages of film preparation. In all cases high quality sapphire substrates were used for films from which I.R. spectra were required.

B. Hydrogen Analysis

Hydrogen analyses were performed on a variety of ion-plated a-Si:H films. Films were prepared with nominal hydrogen pressures ranging from 50 to 200μ . In all the films prepared there was substantial hydrogen, in general greater than 7 a/o. Due to the difficulty in obtaining accurate hydrogen contents there was no systematic variation in hydrogen content with nominal hydrogen pressure. Suffice it to say that there is substantial hydrogen incorporation in the ion-plated films. This is borne out by the electrical conductivity measurements discussed in subsection E.

Figure 3. Percent transmittance vs. wavenumber for an a-Si thin film produced using a 10% silane-argon gas pressure of 0.4 microns

Figure 4. Percent transmittance vs. wavenumber for an a-Si thin film produced using a 10% silane-argon gas pressure of 1 micron

C. Electron Spin Resonance

Electron spin resonance measurements were carried out on hydrogenated amorphous silicon and on evaporated unhydrogenated amorphous silicon films. The results indicate dramatically the effects of hydrogen incorporation on reducing the number of unpaired electron spins or reducing the density of defects in the material. The results for a-Si:H and an unhydrogenated a-Si sample are compared in Figure 5. The number of measurable defects between the hydrogenated and unhydrogenated samples are in the ratio of 1:25.

The films were prepared by deposition onto the NaCl substrates. They were removed from the substrates by floating off in distilled water, and subsequently washed and dried with acetone and methanol.

D. Optical Properties

The optical absorption edges of the a-Si:H were determined using the method of Freeman and Paul. Transmittance versus wavelength data were obtained using a Beckmann-DK-2A optical spectrophotometer.

Optical absorption edges were obtained by plotting $(\alpha h\nu)^{1/2}$ as a function of $h\nu$. A typical plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for an a-Si:H is shown in Figure 6. The observed absorption edges fall predominantly in the range reported by other investigators (Zanzucchi et al., 1977, Loveland et al., 1973), between 1.7 and 1.9 eV. Note that magnetic field confinement of glow discharge produced films does not appear to have any systematic effect on observed optical band gaps.

Fully hydrogenated a-Si:H films prepared by ion-plating were subject to thermal treatment in vacuo at temperatures up to 400°C. The heat treatments produced no observable change in the optical absorption edges. This is in contrast to the behavior exhibited by hydrogenated amorphous boron prepared by glow discharge decomposition of diborane.

Figure 5. ESR spectra of unhydrogenated and hydrogenated a-Si

Figure 6. $h\nu$ vs. $(\alpha h\nu)^{\frac{1}{2}}$ for typical a-Si:H films

E. Dark Conductivity

In unhydrogenated a:Si and a:Ge the high density of localized defect states in the pseudogap makes these semiconductors insensitive to doping (Spear, 1977). Such defect states are drastically reduced by hydrogenation, as in the case of material produced by glow discharge decomposition of silane (SiH_4) or germane (GeH_4), or by r.f. sputtering of silicon or germanium in argon-hydrogen mixtures (LeComber, 1977; Paul, 1976) for example, dopant effects are considerable. Both phosphorous and boron have been successfully used to dope hydrogenated amorphous silicon (a-Si:H) n-type and p-type (Rehm, 1977) respectively, with the observed changes in conductivity varying over several orders of magnitude (Paul, 1976; Rehm, 1977). In almost all of the studies involving substitutional dopants the dopant is introduced through the gas phase using either phosphine (PH_3) or diborane (B_2H_6). Interstitial dopants such as lithium, a donor atom, have also been added by in-diffusion or by ion-implantation (Beyer, 1977). Recently, a method for the preparation of fully hydrogenated amorphous silicon, by evaporation of elemental silicon through a hydrogen plasma has been described (Cocks, 1980). This method lends itself to the introduction of the dopant by co-evaporation. By using co-evaporation doping, elements for which a suitable gas hydride does not exist can be readily used as dopants. The co-evaporation of bismuth and germanium was employed by Vass (Vass, 1974) to prepare bismuth doped unhydrogenated amorphous germanium thin films. Since these films were non-hydrogenated a relatively high concentration of bismuth, typically greater than 1 at % was required to obtain noticeable resistivity effects. Thermopower measurements indicated in this case that the doped films were n-type and the $\ln \sigma$ versus $1/T$ relationship showed the usual linear region above room temperature. Co-evaporation has been used to dope unhydrogenated a:Si with Indium (Mader, 1965).

All films were prepared using the modified ion plating apparatus. The nominal hydrogen pressure in the system during film deposition was 100μ for all films, and the substrate temperature ranged from 300 to 350°C . Doping with yellow phosphorous or 99.99% bismuth was accomplished by co-evaporation from a separate BeO crucible resistively heated by a tungsten filament boat. The temperature of the molten dopant in the crucible was calibrated to the boat current by placing a chromel-alumel thermocouple directly in this boat. The partial pressure of the dopant could then be inferred from the boat current. All films were deposited on carefully cleaned quartz substrates.

D.C. electrical conductivity measurements were made using the standard four point probe technique. Silver of good purity (99.995%) was evaporated onto the films for electrical contacts. The current contacts were 23 mm apart and the voltage contacts 3 mm apart. All conductivity measurements were made in an evacuated system. Even so, in order to avoid problems associated with absorbed moisture, samples were cycled to 120°C in the evacuated apparatus prior to conductivity measurements. The temperature range over which resistivity measurements could be made was from -160°C to 150°C . A Keithly 200B electrometer measured voltage, and a Keithly 409 picoammeter measured current.

The results of the conductivity versus temperature measurements are shown in Fig. 7. On the same figure the results for an evaporated non-hydrogenated-undoped and a fully hydrogenated-undoped amorphous silicon film are given. As is reasonably expected the a-Si:H undoped film had the lowest conductivity while the evaporated a-Si undoped film had the highest conductivity. It is interesting to note that although the a-Si:H films were evaporated from a base pressure of 2×10^{-6} torr the conductivity behavior of the the films closely resembles that of glow discharge decomposed silane (SiH_4) prepared from a base pressure of 4×10^{-7} torr (Zemek, 1980).

Figure 7. Dark conductivity as a function of temperature

Our a-Si:H films also did not exhibit the high conductivity and low activation energy for conduction (0.48 eV) shown by a-Si:H films prepared by SiH_4 decomposition in the presence of a controlled air leak of 2.4×10^{-6} torr. The a-Si:H-undoped film shown in Fig. 7 has a temperature independent activation energy of 0.82 eV, and a 320°K conductivity ($\sigma(320^\circ\text{K})$) of less than $1 \times 10^{-10} (\text{ohm-cm})^{-1}$, and an activation energy for conduction of 0.47 eV. The conductivity data for the phosphorous and bismuth doped samples in Fig.7 show an increase in conductivity at all but the highest temperatures over the fully hydrogenated film. The phosphorous doped film was prepared by co-evaporation of phosphorous from a crucible at 30°C. This temperature would imply an equilibrium partial pressure of yellow phosphorous of 10^{-4} torr. Phosphorous doping reduces the activation energy to .30 eV indicating the Fermi level has shifted from the midgap region and is now close to the band tail states. Similar behavior is observed for the bismuth doped film. In this case the bismuth crucible temperature was maintained at 475°C implying an equilibrium partial pressure of 1×10^{-5} torr. The conductivity $\sigma(320^\circ\text{K})$ was $1.0 \times 10^{-10} (\text{ohm-cm})^{-1}$ and the activation energy 0.65 eV.

On the majority of films tested an initial hysteresis was observed between the heating and cooling cycle. In general the conductivities of the films were higher, often by an order of magnitude, during the initial heating to 120-150°C than they were during cooling to room temperature. We have ascribed this effect to desorption of moisture and other contaminants during heating. It has been observed previously by Zemek, et al. (Zemek, 1980) in lithium doped a-Si:H prepared by plasma decomposition of silane. They attribute the irreversibility to a reaction between lithium and oxygen present in the surface layer.

The optical absorption edge was derived from optical measurements using the method of (Freeman, 1979). The absorption edges in undoped a-Si:H films prepared in this

laboratory generally range between 1.7-1.9 eV. In Fig. 8 the extrapolated absorption edges for an undoped a-Si:H film and the absorption edges for the phosphorous and bismuth doped films from Fig. 7 are shown. In all cases it was observed that doping tended to decrease the optical absorption edge some 0.1 - 0.2 eV. The same effect, although far more pronounced, is observed in lithium doped a-Si:H (Zemek, 1980).

We conclude that co-evaporation of donor elements can be used successfully to dope a-Si:H. the effects of both phosphorous and bismuth doping are to increase R.T. dark conductivity of a-Si:H by approximately 2 orders of magnitude. The linear dependence of $\ln \sigma$ with $1/T$ observed for the doped films over the entire range of measurement is typical of that observed in most lightly doped a-Si:H (Jones, 1977). Based on the results of other studies it can be assumed that the conductivity is n-type (Faul, 1976).

V. X-RAY METHOD FOR THICKNESS AND HYDROGEN CONTENT DETERMINATION

Conventional means of measuring density, as by direct weighing methods, can suffer in accuracy because amorphous silicon films have been noted to adsorb significant amounts of water on their surfaces (Jones, 1979). The weights of typical films (generally one micron in thickness) are quite small (about 0.2 mg/cm^2).

In the present work, the ratio of the intensity of the x-ray fluorescent radiation from bare titanium substrates coated with hydrogenated amorphous silicon thin films have been measured. The ratio of the total integrated x-ray fluorescence intensity of the substrate material with and without a film are used to calculate the mass area density of silicon present in the film. By accurately measuring the thickness, both the density and the total amount of silicon present can be closely estimated due to the small contribution of any hydrogen present to either the total film mass or to the observed absorption of the fluorescent radiation from the substrate.

Figure 8. $\sqrt{\alpha h\nu}$ vs. $h\nu$ for P doped, Bi doped and undoped a-Si:H

If desired, the effect of hydrogen on both density and x-ray absorption can be taken into account by iteration.

This method of measuring film densities has several advantages over conventional pycnometric, flotation, or other techniques. First, with the proper choice of substrate the resulting absorption of the fluorescent radiating measurement even in thin ($\sim 1\mu$) films is sufficiently large that mass area densities are limited in accuracy only by the thickness measurement. Second, the intensity of the x-ray fluorescence is insensitive to the presence of adsorbed water on the film. Third, the method is completely non-destructive. Similar methods have been applied before, both to the measurement of the thickness of Al thin films on Si (Cline, 1967) and the analysis of InSb thin films (Hartley, 1978).

For any homogeneous material, the fractional decrease in x-ray intensity passing through the material is given by the well known absorption equation:

$$I = I_0 \exp\{-\mu t\} \quad (1)$$

where I_0 is the intensity of the incident radiation, I is the intensity of the transmitted radiation, t is the thickness of the material, and μ is the linear absorption coefficient, which depends upon both the x-ray wavelength and the absorber material. Values of μ are typically reported for different characteristic x-ray wavelengths for the case of absorption by pure elemental materials*. For alloys or compounds (in the present case amorphous hydrogenated silicon) the absorption coefficient must be corrected for the reduced density of silicon atoms present per unit volume as compared to that of pure crystalline silicon. This correction is made by rewriting Eq. (1) as:

$$I = I_0 \exp\left\{-\left(\frac{\mu}{\rho_0}\right)\rho_f t\right\} \quad (2)$$

*International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, England (1974) 61.

where ρ_0 is the density of the pure substance (2.33 g/cm^3 for pure silicon) and ρ_f is the actual density of silicon present in the absorbing film. The other elements present in the film, in this case hydrogen, will also act to decrease the intensity and to include this contribution. Eq. (2) can be rewritten as:

$$I = I_0 \exp\left\{-\left[\left(\frac{\mu}{\rho_0}\right) \rho_f S_i + \left(\frac{\mu}{\rho_0}\right) \rho_f H\right]t\right\} \quad (3)$$

In the present case the hydrogen absorption can be initially neglected since not only is the mass absorption coefficient for hydrogen small, but in addition the density of hydrogen in the film is also small. For Mo $K\alpha$ radiation $\left(\frac{\mu}{\rho_0}\right)_H$ is only $0.3727 \text{ cm}^2/\text{g}$ (Cline, 1967). Fig. 9 shows the physical arrangement as it applies to the present method.

When the incident x-ray beam of intensity I_0 strikes the substrate, this substrate will fluoresce at characteristic wavelengths, dependent on its composition. For a substrate having no thin film, the intensity of the resultant fluorescent radiation, I_F^0 , from a given element in the substrate can be considered to be directly proportional to the incident intensity with $I_F^0 = KI_0$.

However, for a film-covered substrate, the incident x-ray beam of intensity I_0 must first pass through the film and thus its intensity, as incident on the substrate, will be reduced by absorption in the film. Since the incident beam wavelength is short and the concomitant mass absorption coefficients small, this correction is also small, though not negligible (typically 6%). For Mo $K\alpha$ excitation radiation the reduced intensity I'_0 incident upon the substrate beneath the film will be given by (from Fig. 9)

$$I'_0 = I_0 \exp\left\{-\left(\frac{\mu}{\rho_0}\right) \rho S_i \frac{t}{\sin \theta}\right\} \quad (4)$$

where the mass absorption coefficient is that for the incident radiation, in this case Mo K α ($\lambda = .7107\text{\AA}$ and $(\frac{\mu}{\rho_0})_{S_i} = 6.533$). As before, the absorption of this incident radiation by hydrogen is neglected, as is the air path length differences between film covered and bare substrates ($\sim 1\mu$).

Once the incident beam of intensity I'_0 strikes the metal substrate, the intensity of fluorescence, I_F , will be directly proportional to this incident intensity with $I_F = KI'_0$. This fluorescent radiation must then traverse a film thickness t_2 . From Fig. 9 this thickness, t_2 , is simply given by $t/\cos \theta$. As for the incident beam, this fluorescent radiation will be reduced in intensity by passage through the film. Therefore, the intensity outside the film of the outgoing fluorescent beam is given (in the case of titanium substrate) by:

$$I'_F = I_F \exp \left\{ - \left(\frac{\mu}{\rho_0} \rho_f \right)_{S_i} \frac{t}{\cos \theta} \right\} \quad (5)$$

where in the present case (μ/ρ_0) is the mass absorption coefficient of pure silicon for Ti K α radiation ($336.0 \frac{\text{cm}^2}{\text{g}}$). Again, as before, the mass absorption coefficient of hydrogen for titanium K α radiation ($0.4323 \text{ cm}^2/\text{g}$) is neglected. It should be noted that this low value is still further reduced by the low value of the density (g/cm^3) of hydrogen in the film.

Using the value of I'_0 from Eq. (4) and taking the ratio of the fluorescent intensity with and without the film present yields the observed ratio, R , of the fluorescent intensity from the film covered titanium substrate to that of the bare substrate as:

$$R = \frac{I'_F}{I_F} = \exp \left\{ - \rho_f t \left[\left(\frac{\mu}{\rho_0} \right)_{S_i}^{\text{MoK}\alpha} \left(\frac{1}{\sin \theta} \right) + \left(\frac{\mu}{\rho_0} \right)_{S_i}^{\text{TiK}\alpha} \left(\frac{1}{\cos \theta} \right) \right] \right\} \quad (6)$$

Eq. (6) shows that the observed intensity ratio will depend not only on film thickness and substrate material but will depend as well on the angle of the incident x-ray

beam with respect to the substrate. The variation of this ratio for a series of substrate materials for the fixed angle of 45° , as a function of the silicon mass area density assumed present in the film is shown in Fig. 10, while Fig. 11 shows the variation in this ratio as a function of substrate angle for these same substrate materials at the constant mass area density corresponding to a pure crystalline silicon film 1μ thick.

These figures show that the sensitivity of this method decreases, as expected, with increasing atomic number of the fluorescing element being considered in the substrate. If stainless steel substrates, not titanium substrates, had been used, Cr would be the preferred element on which to base the calculation of the quantity $(tp_f)_{S_i}$ in Eq. (6). Whether Ti or a Cr-containing substrate is used, however, the expected error in the determination of the ratio R is, of course, dependent on the total counts recorded for each integrated total intensity measurement. This total integrated intensity can easily be made as high as 10^6 counts or more, however leading to a counting error of 0.1% or less. This error would then lead (for $R = 0.7$) to an error of only $.0021 \text{ mg/cm}^2$ in the value of the mass of silicon per unit area of the film. Furthermore if desired, based on the initially calculated hydrogen content, a correction for hydrogen absorption can easily be made and the $(tp_f)_{S_i}$ value recomputed.

Another slightly different method in which x-ray fluorescence could be used to obtain the mass area density of hydrogenated amorphous silicon thin films is as follows. If, instead of obtaining the absorption ratio for a single fluorescent peak, R , as described above, the absorption ratio for two fluorescence peaks R_1 and R_2 , could be measured and the ratio of the ratios, R_1/R_2 , used to measure film area density. This procedure would eliminate any error in measurement due to possible

Figure 10. Intensity ratio, R , versus film area density calculated assuming a substrate angle of 45°

Figure 11. Intensity ratio, R , versus substrate angle calculated using a constant film area density of 0.233 mg/cm^2 , corresponding to a layer of crystalline, unhydrogenated silicon one micron thick.

slight variations in the substrate angle θ , since any deviation in the angular orientation of the samples with and without films will be taken into account through the relative ratios of the respective $K\alpha$ and $K\beta$ intensities.

As an example, for titanium substrates, this technique could be applied to $TiK\alpha$ and $TiK\beta$ fluorescence. Thus

$$R_1 = \left(\frac{I'_F}{I_F} \right)_{TiK\alpha} \quad (7)$$

and

$$R_2 = \left(\frac{I'_F}{I_F} \right)_{TiK\beta} \quad (8)$$

and taking the ratios of the absorption ratios

$$\frac{R_1}{R_2} = \frac{(I'_F/I_F)_{TiK\alpha}}{(I'_F/I_F)_{TiK\beta}} \quad (9)$$

Because the mass absorption coefficients in silicon for $TiK\alpha$ is larger than that for $TiK\beta$ (336.0 vs. 262.9), R_1/R_2 will be less than 1.00, and the thicker the film the larger the reduction in the ratio of Eq. 9.

This effect is shown in Fig.12 for both titanium ($TiK\alpha/TiK\beta$) and 18-8 stainless steel ($\frac{CrK\alpha}{FeK\alpha}$, $\frac{CrK\alpha}{NiK\alpha}$, $\frac{CrK\alpha}{CrK\beta}$) substrate materials using the density of crystalline silicon and a substrate angle of 45° . Fig.13 shows calculated variations in R_1/R_2 as a function of substrate angle using the same possible combinations of fluorescence peaks for titanium and 18-8 stainless steel (Type 304) substrate material and assuming a 1 micron thick film of crystalline silicon. Note that although the ratio-ratio technique eliminates any systematic error due to possible misalignment of the substrate in moving from a bare to a coated area, for identical conditions the absorption ratio (R_1/R_2) will be less sensitive to changes in film thickness than for the simple absorption ratio (R) procedure due to the fact that the difference between

Figure 12. Intensity ratio-ratio, R_1/R_2 , versus film area density calculated assuming a substrate angle of 45°

Figure 13. Intensity ratio-ratio, R_1/R_2 , versus substrate angle calculated using a constant film area density of 0.233 mg/cm^2 , corresponding to a layer of crystalline, unhydrogenated silicon one micron thick

the mass absorption coefficients for $K\alpha$ and $K\beta$ radiation will necessarily be smaller than the mass absorption coefficient for $K\alpha$ radiation itself. Thus, even though possible errors due to slight misalignment of the substrate could be eliminated, the inherent accuracy of this method is somewhat reduced.

The present technique was applied to hydrogenated amorphous silicon prepared by glow discharge decomposition of silane. Films were produced using a gas mixture of approximately 40 volume percent SiH_4 and H_2 , and a glow discharge current density of approximately 10 ma/cm^2 . Films were deposited on unheated titanium substrates at a rate of $\sim 4.2 \text{ \AA/sec}$. The titanium substrates were masked so that the resulting film covered approximately half of the substrate, which makes possible the measurement of the x-ray fluorescence intensity, R , from a single sample.

X-ray measurements were made using the standard x-ray fluorescent geometry together with a molybdenum target x-ray tube. Ti- $K\alpha$ fluorescent peaks as a function of 2θ were obtained by point counting for a fixed time interval (100 sec) at small increments ($.02^\circ$) of $\Delta 2\theta$ thus allowing the direct determination of integrated total intensity with accurate background correction.

The thicknesses of the films were measured to within ± 0.01 microns using a Bendix Proficorder profilometer. These thickness values were subsequently used to calculate the density of the films (with respect to Si) from the measured Si mass area density, $(\rho_f t)$ values.

Titanium was chosen as the substrate material because of the refractory metal elements which might be considered as substrate materials, titanium possesses the longest wavelength $K\alpha$ fluorescent radiation and concomitantly shows the highest mass absorption coefficient in silicon ($336.0 \text{ cm}^2/\text{gram}$). Thus, as shown in Fig. 10, for a given film thickness the intensity ratio, $R = \frac{I'_F}{I_F}$, will display the greatest change and hence sensitivity for Ti- $K\alpha$ radiation. For a film with a thickness of

3.38 microns, the measured ratio I_F'/I_F was determined to be 0.700. The calculated mass area density ($\rho_f t$) of silicon for this film is then 0.7363 mg/cm^2 . This calculated value can be expected to have a relative error of 0.2% since 2.46×10^5 total integrated counts were used in obtaining intensity ratios. The absolute values will, of course, be only as accurate as the values used for the mass absorption coefficient (which could be as high as 2%). However, the relative error in these measurements will be far less since the relative error would be previously determined by the counting error and this can be made small by using larger integrated total intensities. If this film were pure crystalline silicon its thickness would therefore be 3.16 microns. Since the measured thickness was 3.38 microns, the density of this film, neglecting the weight of hydrogen is therefore $(\rho_f t)/t = (0.7363 \times 10^{-3})/(3.38 \times 10^{-4}) = 2.18 \text{ g/cm}^3$. When this number is compared to published values of the density, the hydrogen content can be estimated at 13 a/o. The present method can be expected to contribute to the development of such data produced by the different methods that are available. With the value of 13 atomic percent for the hydrogen content, the corrected absorption data including the effects of this hydrogen in x-ray absorption gives a newly calculated silicon mass per unit area that is affected only in the fifth decimal place from that calculated previously, thus justifying the previous assertion that the effect of hydrogen on such x-ray absorption can be ignored.

Using the value of 13 atomic percent hydrogen, together with the measured value of 3.38 microns for the thickness yields the corrected value (corrected to include the weight of this hydrogen) for the density of this hydrogenated amorphous silicon film as $2.19 \pm .017 \text{ g/cm}^3$. The available data relating density to hydrogen content are not sufficiently accurate to permit a second iteration of hydrogen content to be made based on this corrected density.

By comparing the $TiK\alpha$ fluorescent radiation intensity ratios obtained from both bare titanium substrates, and titanium substrates coated with amorphous hydrogenated silicon thin films, an accurate value of the mass area density (ρ_{ft}) of silicon in these films can be calculated. Dividing this mass area density by film thickness gives an estimate of the density of these films. The hydrogen content of these films can be estimated from this initial density measurement and this hydrogen content used to make a small (typically 1%) correction to the value obtained accounting for silicon alone. Because integrated total intensity measurements can be made with a very high degree of relative accuracy, the use of this present method to determine the mass of silicon in a film may be preferred to simple weighing methods even when hydrogen is subsequently determined by gas evolution methods. Hydrogen determinations based on resonant nuclear reaction methods or infrared absorption methods require calibration samples of known hydrogen content. Such standards are usually based on gas evolution results which in turn depend, for the reporting of hydrogen atomic percentages, on weight measurements of the original films as well as direct hydrogen determination, usually by mass spectrographic or non-condensable gas methods. The use of silicon determination by the x-ray absorption method reported here may help to improve the accuracy of such standard samples, as well as to provide useful information of the kinetics of silicon by different film preparation techniques.

VI. STRAIN MEASUREMENTS

The problem of adhesion and residual stresses in corrosion and wear resistant coatings has been known for a long time (Stoney 1909; Bronner, 1949; Treahing, 1951) but the problem in electronic coatings (such as semiconductors) is a more recent one (Deesler, 1979; Koos, 1976; Kinoshita, 1965). Some available experimental data indicates that high stresses (100 - 1000 MPa; 1500-150,000 psi) may even affect the energy band structure and consequently the electrical properties of the semiconductor (Wortmann, 1965).

In the present work thin amorphous Si-films have been deposited on various thin substrate strips from glow discharge of silane and the curvature of the strip is being used to evaluate the magnitude of their stress. These experiments have shown that compressive stress as high as 17,000 psi can be produced and further work is underway to study the effects of the substrate temperature and to explain some observed phenomena.

VII. CONCLUSIONS

Ion plating has been shown to be able to produce hydrogenated amorphous silicon thin films. Furthermore, as has been found traditionally in ion-plating, a-Si:H films produced by ion plating appear to be considerably more adherent than films produced by glow discharge decomposition. Increased film adherence is, in fact, one of the main reasons why ion plating is used industrially (as in the metallizing of plastic materials). Hydrogenated amorphous Si films produced by ion-plating show all of the primary infrared absorption effects found for glow discharge produced films. Electron spin resonance measurements confirm that the incorporated hydrogen acts to dramatically reduce the number of unpaired electron spins. Optical band gap measurements show gaps ranging from 1.6 to 1.9 eV. Electrical conductivity measurements confirm a substantial reduction in the density of defect states in the gap of hydrogenated as opposed to unhydrogenated ion-plated films, as expected. It has also been shown that hydrogenated amorphous silicon prepared by ion-plating can be doped by co-evaporation of the dopant during film deposition. Both co-evaporated bismuth and phosphorous have been found to substantially decrease the dark conductivity while shifting the other Fermi levels towards the conduction band edge.

An x-ray method for estimating the density and hydrogen content of a-Si:H has been developed and a method for the measurement of strain in a-Si:H films is described.

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