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

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Abstract

Using quartz substrates, hydrogenated a-Si thin films have now been produced both by glow discharge decomposition of silane and by the controlled ion plating of high purity silicon through glow discharges composed of silane, hydrogen, and argon using a modified Takagi appratus. Thus far, thin films produced by both glow discharge decomposition of silane with and without magnetic confinement and by ion plating have been characterized and compared using x-ray deffractometry, infrared spectroscopy, optical absorption spectroscopy and by their temperature dependence of resistivity. Based on these results, the ion plating technique of producing a-Si thin films looks extremely encouraging. Films have been produced at approximately ten times the deposition rate obtained using glow discharge decomposition of silane, even with magnetic field containment. In addition the resulting thin film properties measured to date compare favorably with those obtained from our glow discharge produced films and the properties of glow discharge produced films reported in the literature.

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 (Takagi, et al, 1978, Takagi, et al, 1976). In their experiments the ionizing vapor was composed of thermionically generated electrons rather than the more usual use of evaporation into a glow discharge. 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.

This program has as its primary goal the development of methods for the preparation of efficient, low cost amorphous thin film solar cells involving the direct use of the ion plating technique.

As discussed in our first quarterly report, the first three months of this research program was devoted to the modification of our ion plating apparatus to permit the introduction of silane and dopant gasses into the glow region, and to the optimization of the glow discharge plasma and the concomitant deposition rate by the use of magnetic fields. During the last reporting period we have focussed our efforts on the preparation of thin films by the controlled evaporation of high purity silicon into glow discharges composed of silane, hydrogen and argon using our modified Takagi apparatus, and on the characterization of the thin films produced using magnetic containment and ion plating techniques.

Experimental Program

A. Film Preparation

Two oil-pumped vacuum systems have been modified to produce a-Si thin films by the combined glow discharge decomposition of silane and ion plating techniques. Both systems are capable of being pumped to 10^{-7} torr by using liquid nitrogen baffles to eliminate backstreaming.

The glow discharge system has been 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 has been 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 indicate that magnetic containment can be used to more than double the deposition rate at a given power input.

Ion plated films are currently being produced using a modified Takagi ion cluster apparatus. In this system a silicon charge is evaporated by using an RF heating coil and the evaporated silicon is allowed to adiabatically expand into a glowing gas. Films have been produced using hydrogen and a mixture of 10% Si in argon as a glow medium. Silicon films were also produced by evaporation through a glow of argon alone to establish base-line ion plating parameters. First, it was necessary to determine the evaporation parameters required to allow for silicon to evaporate during the entire time period (~1/2 hr.) required to produce ~1μ silicon film from the glow discharge decomposition of silane alone. Second, based on the mass of the silicon charge used, it was necessary to determine exactly what fraction of the evaporated silicon was actually deposited on the substrate. This is a function not only of the mass of the silicon charge and the length of the evaporation period, but also of the gas pressure used for glow discharge decomposition. As the glow pressure is increased, the mean free path of evaporated silicon atoms is reduced, hence, fewer silicon atoms reach the substrate. Results to date indicate that approximately 15% of the silicon charge reaches the substrate when the glow pressure is 100μ and that, with our present configuration, the rate of silicon evaporation can be controlled sufficiently as to allow for 30 minutes of continuous evaporation.

Hydrogenated a-Si thin films have been produced by ion plating in a silane glow. Initially, our efforts were focused on obtaining ~1μ thick adherent deposits so that the electrical and optical properties of the resulting thin films could be measured and compared to those obtained from the glow discharge decomposition of silane alone.

We have produced such films at approximately ten times the rate at which we are able to produce a-Si films by glow discharge techniques. In analogy with the production of hydrogenated a-Si films by reactive sputtering (Brodsky, et al, 1977A) it is apparent that in studying the effect of SiH_4/H_2 ratio, experiments must also be done with this ratio at zero; that is without silane. If it is indeed possible to produce hydrogenated a-Si by ion plating through hydrogen alone a considerable number of attractive possibilities will have been opened up, not the least of which would be the elimination of the hazards involved in the handling of silane. We expect to begin such experiments shortly.

X-ray diffractometry was performed on several films produced by the glow discharge decomposition of silane and ion plating. Diffraction patterns were obtained both on as-deposited films and on films that had been heated in a vacuum furnace for one hour over a range of temperatures. As-deposited films and those heated to above 700°C gave no distinct peaks, while the same films heated to above 700°C exhibited diffraction peaks corresponding to the (111), (220) and (311) planes of crystalline silicon. This implies that the crystallization temperature of our amorphous silicon thin films produced by both glow discharge decomposition and ion plating is 700°C. This observation is consistent with crystallization temperatures reported in the literature for a-Si thin films. (Herd, et. al., 1972).

B. Film Evaluation

In the following subsections, IR spectra, electrical band gaps, and optical band gaps obtained from a-Si films produced by glow discharge decomposition of silane both with and without magnetic confinement and by ion plating are compared.

IR Spectrometry

Typical infrared absorption spectra obtained from glow discharged produced a-Si thin films are shown in Figures 1 and 2. The spectrum shown in Figure 1 was obtained using a 10% silane-argon gas mixture at a pressure of 0.40 torr and a voltage and glow current of 900V and 10 ma, respectively. The absorption peak located at a wavenumber of ~2090 cm^{-1} is due to a stretching mode associated with SiH_2, while the peak at a wavenumber of ~2000 cm^{-1} is associated with

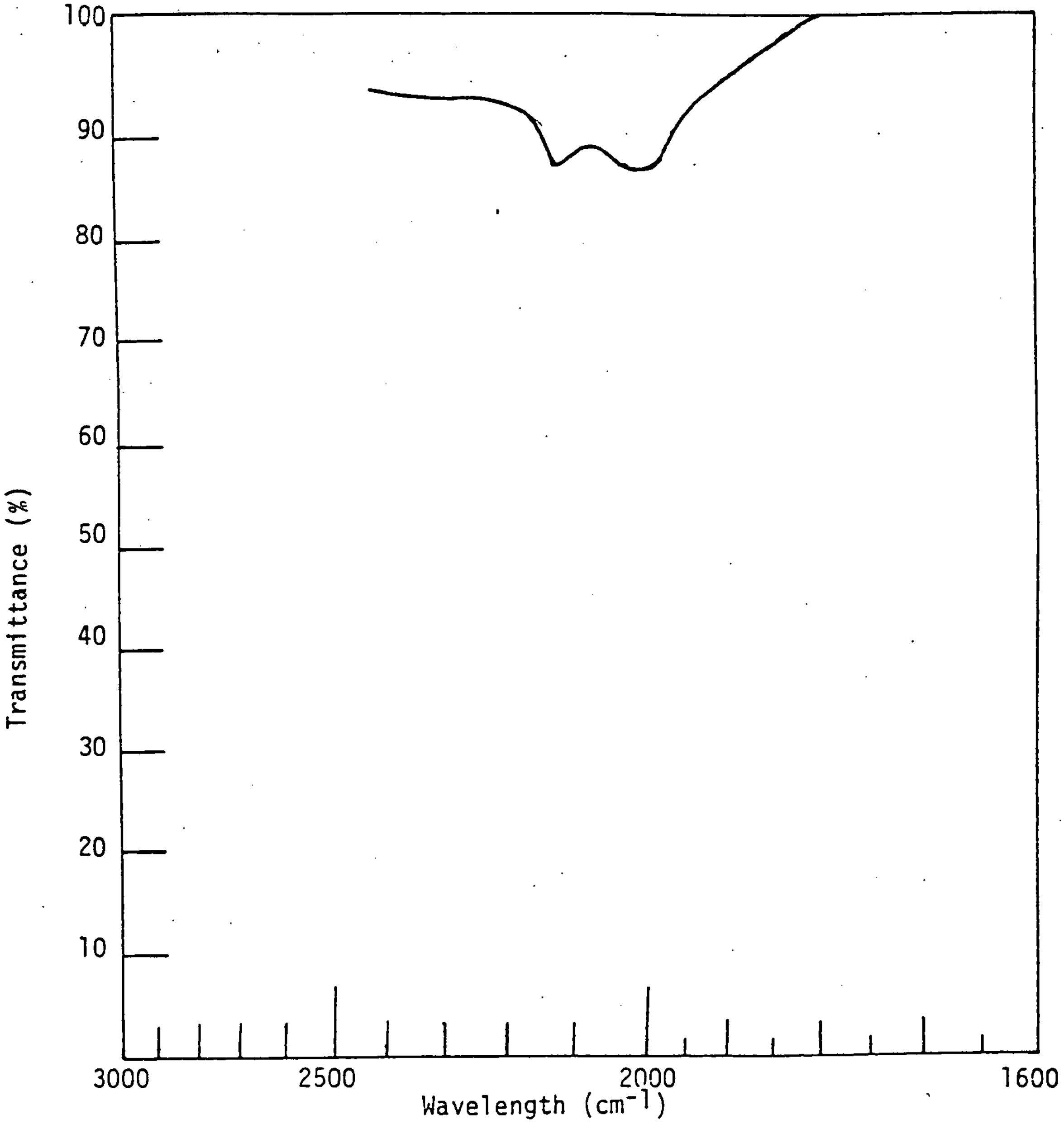

Figure 1: Percent transmittance vs. wavenumber for an a-Si thin film produced using a 10% silane-argon gas pressure of ~0.4μ.

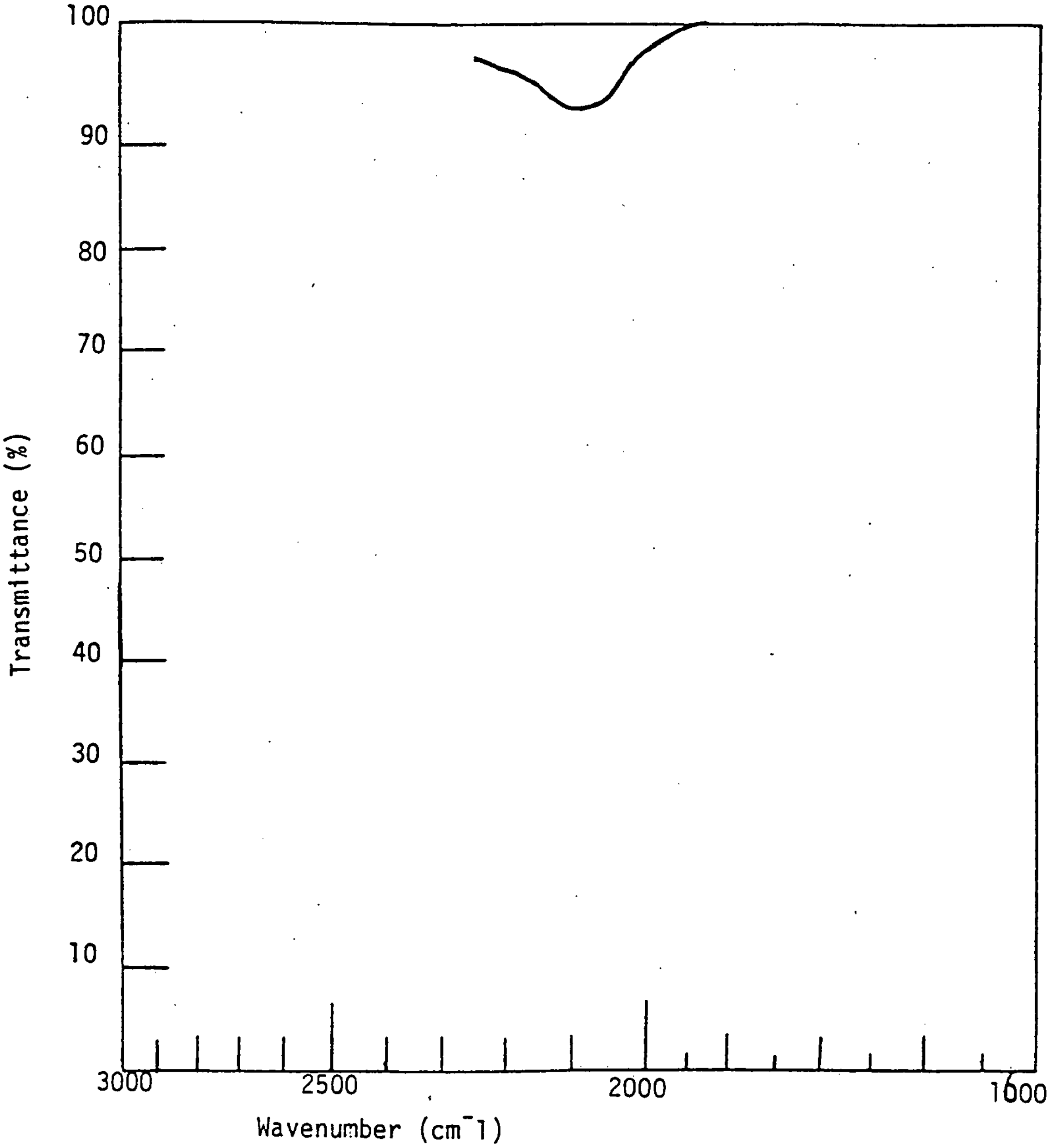

Figure 2: Percent transmittance vs. wavenumber for an a-Si thin film produced using a 10% silane-argon gas pressure of ~1μ.

the SiH stretching mode (Tsai, et. al., 1977). The spectrum shown in Figure 2 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 ~2090 cm^{-1} which corresponds to SiH_2 stretching. This result is consistent with observations made by Brodsky (1977B).

The film used to generate the spectrum shown in Figure 1 was produced at a lower gas pressure and was red and adherent. The spectrum shown in Figure 2 was obtained from a film produced at a higher gas pressure and was yellow in appearance, consistent with the known result that by varying the glow pressure, films can be produced with varying amounts of SiH and SiH_2 bonding.

Resistivity as a Function of Temperature

Resistivity measurements as a function of temperature have to date been obtained over the temperature range of 294°-338°K. and will shortly be extended to 77°K. These measurements are used to obtain the electrical band gap (E_c - E_f) of the a-Si thin film.

Electrical conductivity can be expressed as an exponential function of temperature by the relation

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

where σ_0 is a constant, k is Boltzman's constant, and ΔE is the energy separation from the bottom of the conduction band to the Fermi level. In this equation ΔE represents one-half of the electrical (as opposed to optical) band gap in the case of intrinsic semiconductor. Measurement of dark electrical conductivity versus temperature permits evaluation of ΔE. Spear and LeComber (1975), have measured ΔE for doped and undoped a-Si and found the undoped material, fabricated from the glow discharge decomposition of silane, to have a ΔE of 0.30-0.95 ev, depending on deposition conditions.

Initial results obtained in this laboratory are shown in Table 1. The a-Si films produced by glow discharge decomposition of silane both with and without magnetic enhancement and the films produced by ion plating in a hydrogen glow discharge exhibit thermal gaps that are consistent with those found by other researchers (Spear and LeComber, 1975; Fritzsche, 1978). Although the thermal gap calculated for the film produced in a magnetic field is different from that produced with no magnetic confinement, both are in the range reported for normal glow discharge of silane produced a-Si films. Further testing is required to determine if the use of magnetic field duirng deposition systematically moves the Fermi level.

It is encouraging to note that the ion plated films tested thus far have thermal gaps similar to those obtained from silane produced films. The increased rate of deposition noted with ion plated films over glow discharge produced films could significantly reduce the costs associated with solar cell production, provided the electronic properties of these films are not inferior.

Optical Band Gap

One of the very real advantages of using a-Si as a photovoltaic material is that it has an absorption coefficient of greater than 10^4 cm^{-1} for wavelengths less than ~0.7 microns (Zanucchi, et al., 1977). This high absorptivity enables, of course, thin (~1μ) films to be effective as cells. In order to be able to make absorptivity measurements we have recently purchased (using Duke funds) a Beckman DK-2A spectrophotometer.

Table 1. Electrical Gaps as a Function of Deposition Technique

Deposition Technique	(E_c-E_f)(eV)
Glow discharge of SiH_4 (no magnetic field)	0.798
Glow discharge of SiH_4 (magnetic field of 0.75 tesla)	0.472
Ion Plated (hydrogen glow)	0.436
Ion Plated (hydrogen glow)	0.435

The measurement of absorptivity for supported thin film materials is not simple, due to the need to account for reflection loses both at the film surface and at the film-substrate interface. There are two principal methods available, however, for such absorptivity measurements. In either case, what is measured experimentally is the transmittance versus wavelength relationship.

In the case of a-Si films deposited on intrinsic crystalline silicon, where the transmittance of the substrate is known ($T_o = 0.54$) and $n_{sub} \cong n_{film}$ the equation

$$T = \frac{4T_o^2 \exp[-\alpha d]}{(1+T_o)^2 - (1-T_o)^2 \exp[-2\alpha d]}$$

where T is the overall transmittance, α is the absorption coefficient and d the film thickness, has been used to convert transmittance data to absorptivity (Brodsky, et al., 1977A). Because the films used in this study were deposited on glass and quartz substrates, the above equation must be generalized. The relationship between absorptivity and transmittance then becomes (Freeman and Paul, 1978)

$$\alpha = -\frac{1}{d} \ln \left| \frac{1}{B} \{A + [A^2 + 2BT(1 - R_2R_3)]^{1/2}\} \right|$$

where

$$A = -(1-R_1)(1-R_2)(1-R_3)$$

$$B = 2T(R_1R_2+R_1R_3-2R_1R_2R_3)$$

$$R_1 = \left(\frac{n-1}{n+1}\right)^2 \qquad R_2 = \left(\frac{n-n_o}{n+n_o}\right)^2 \qquad R_3 = \left(\frac{n_o-1}{n_o+1}\right)^2$$

where n is the index of refraction of the film and n_o that of the substrate.

The method of Yates (1979) has been used to approximate the index of refraction of a-Si thin films deposited on quartz substrates. This technique allows for the calculation of n from observed oscillations in transmittance at long wavelengths due to interference effects using the equation

$$n = \frac{1}{2d(k_2-k_1)}$$

where $k = 1/\lambda$, and $(\lambda_2-\lambda_1)$ represents the difference in wavelength of adjacent minima or maxima in transmittance oscillations. A typical transmittance versus wavelength curve obtained using a-Si films produced in this lab is shown in Figure 3.

Using the technique outlined above absorptivities as a function of wavelength were calculated for a series of a-Si films produced by glow discharge decomposition of silane with magnetic containment. Figure 4 shows for reference the absorptivity versus wavelength relation measured for an a-Si film produced by the decomposition of silane with magnetic containment. This result does not differ materially from that obtained for films produced without magnetic containment of the glow discharge. We are in the process now of carrying out similar measurements on ion-plated films.

Optical gaps have also been obtained by plotting $(\alpha h\nu)^{1/2}$ as a function of $h\nu$. (Spear and LeComber, 1975). A typical plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ is shown in Figure 5. The optical gaps thus obtained for a variety of films are given in Table 2. The observed optical gaps lie predominantly in the range reported by other investigators (Zancucchi et al., 1977; Loveland et al., 1973). Note that magnetic field confinement of glow discharge produced films does not appear to have any systematic effect on observed optical band gaps. Although the ion plated films exhibit the largest optical gap (2.07 ev), further testing must be carried out before a definitive conclusion can be reached since it is known that inhomogenieties in the film can affect the optical gap measured in this manner.

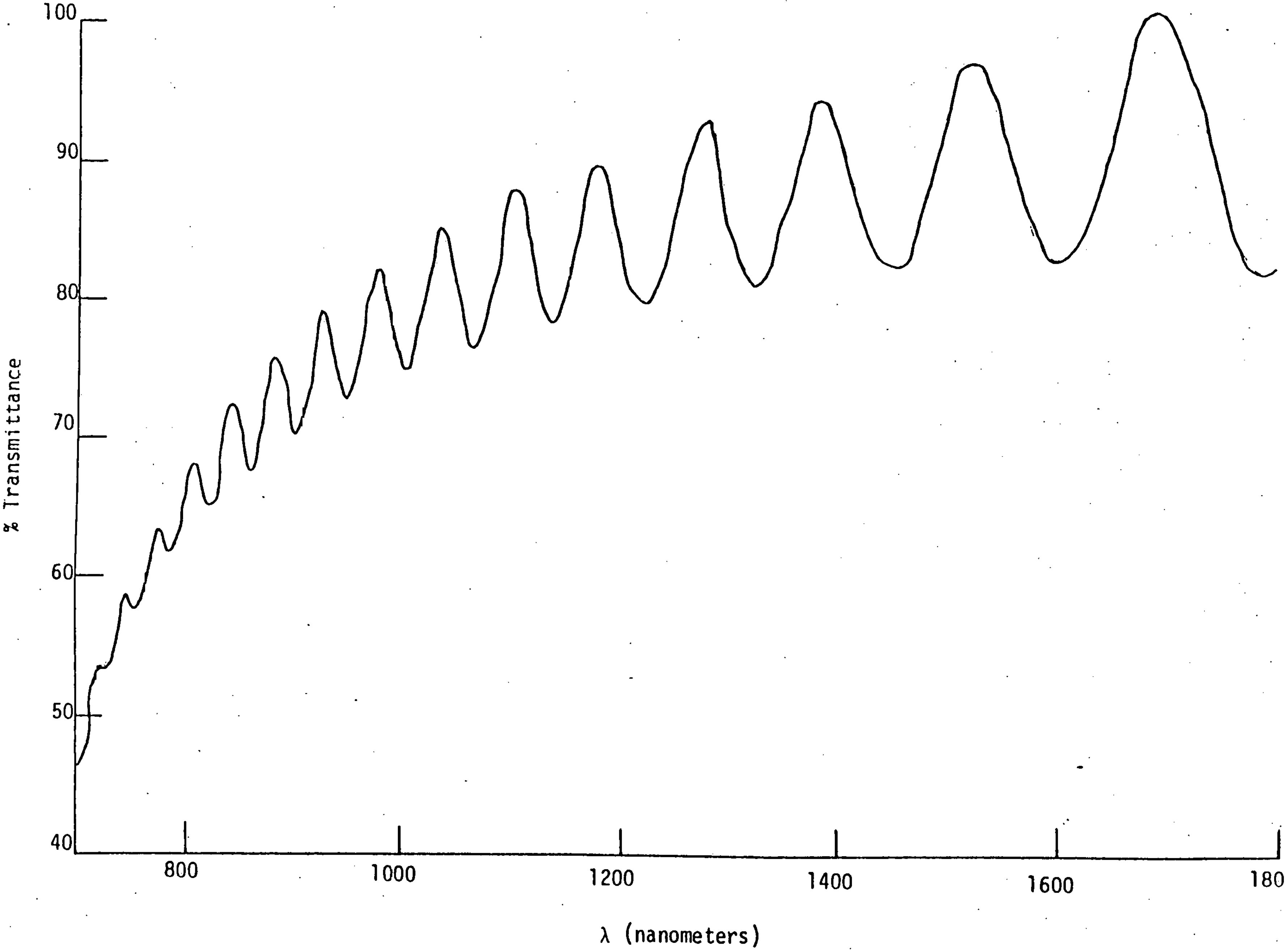

Figure 3: Transmittance versus Wacelength Showing the Optical Interference Effects Used to Measure Index Refraction.

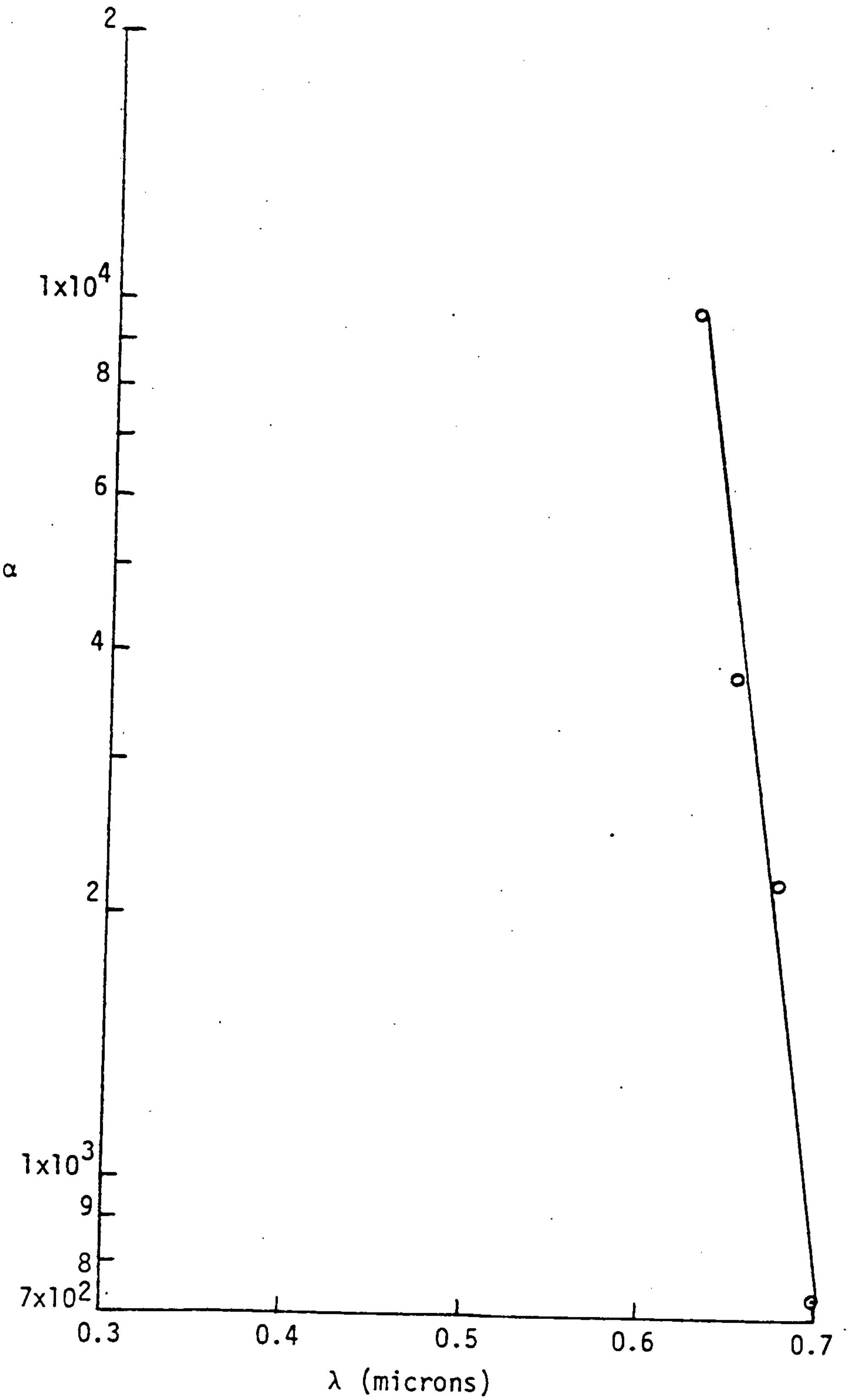

Figure 4: Absorptivity versus wavelength for a-Si produced using magnetic containment.

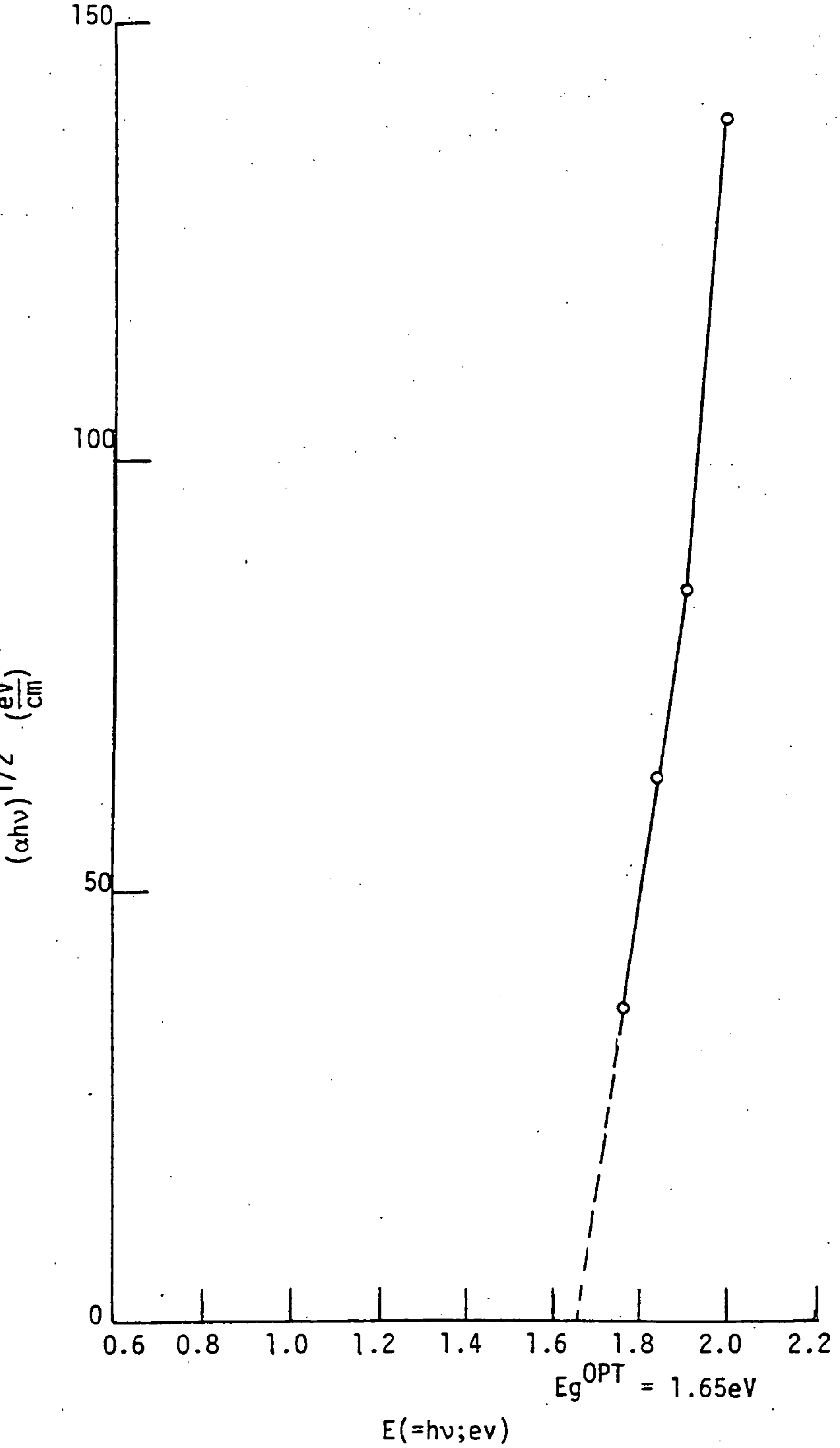

Figure 5: $(\alpha h\nu)^{1/2}$ versus Photon energy

Table 2 Optical Band Gaps as a Function of Deposition Technique

Deposition Technique		Optical Gap (eV)
Glow discharge of SiH_4, no field	(1)	1.38
	(2)	1.55
	(3)	1.38
	(4)	1.65
	(5)	1.85
Glow discharge of SiH_4 (0.5 Tesla)		1.77
(0.75 Tesla)	(1)	1.91
	(2)	1.91
	(3)	1.55
(1,00 Tesla)		1.55
Ion Plated Through H_2	(1)	2.07
	(2)	2.07

Summary

Ion plating techniques have been used to produce a-Si thin films at approximately ten times the deposition rate achieved using glow discharge decomposition of silane alone, even with magnetic containment. The resulting thin film properties measured to date, which include IR spectra, optical band gap, and electrical band gap, compare favorably with those obtained from our glow discharge produced films and the properties of glow discharge produced films reported in the literature.

Future Plans

The thrust of our work through the remainder of the first year is the systematic evaluation of ion plated a-Si properties in our modified Takagi apparatus as a function of preparation conditions (glow current density, gas pressure, evaporation boat temperature, boat-to-substrate separation, and Takagi cell configuration and voltage). The film properties to be studied here include electrical gap, optical gap, absorptivity, photoconductivity, resistivity, absolute hydrogen content, and the average density of localized states (by plotting the reciprocal of the square of the capacitance as a function of applied voltage).

We have presently in hand a large number of a-Si films produced by simple glow discharge decomposition of silane at different magnetic field strengths and these films will be included in the property evaluation tests described above.

As was discussed in the preceding section, we will also investigate the possibility that hydrogenated a-Si films can be produced by ion plating through hydrogen alone, without silane. If this is indeed possible, it would be of compelling interest.

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