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OPTICAL ABSORPTION OF $SiH_{0.16}$ FILMS NEAR THE OPTICAL GAP

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We have made detailed measurements of the optical transmission and reflection in the photon energy range of 0.5 to 5.0 eV on $SiH_{0.16}$ films deposited by discharge decomposition of SiH_4 on quartz substrates held at 240°C. Above 2.0 eV, the spectral dependence of ε_2 is in excellent agreement with a model derived for parabolic bands in a disordered material. The range of coherence is about 20A very close to other materials (a-Si, a-Ge, As_2Se_3). The extrapolated value of the band gap (Eg) is 1.8 eV. Below 1.8 eV we have utilized photoconductivity and optical absorption and have observed an exponential dependence in α to 1.5 eV with an activation energy of 0.06 eV. From 1.5 eV to 1.2 eV absorption occurs to a photoconducting state with a maximum at 1.3 eV.

INTRODUCTION

Amorphous silicon hydride (a-SiH_x) is a new semiconducting material. It is the first thin film material that exhibits a full range of semiconducting properties (optical gap, extended state mobility, doping sensitivity) independent of substrate.[1-2] Current interest in the performance of this material as a thin film photovoltaic[3] enhances the importance of characterizing as fully as possible the semiconducting properties of this interesting new material.

In this paper we focus on the optical properties of films prepared by RF capacitive glow discharge decomposition on anodic substrates held at temperatures above 250°C (RFGD films).

The optical properties of the film, the complex index $\tilde{N}$ ($\tilde{N} = n + i\kappa$) and dielectric constant $\tilde{\varepsilon}$ ($\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 = \tilde{N}^2$) were measured by transmission and reflection (with respect to c-Si). At very low energies, we utilized the film photoconductivity normalized to the transmission measurements at a photon energy of 1.75 eV. Hydrogen concentrations were determined by the N^{15} resonance reaction[4] as well as by calibrated measurements of the integrated absorption in the Si-H stretch vibration at 2000 cm^{-1}.

The major interest of the paper is the spectral dependence of the optical absorption constant $\alpha(\alpha = 4\pi\kappa/\lambda)$ in the three energy regions: $E > E_G$; $E \sim E_G$; and $E < E_G$, where E is the energy of the incident light and E_G is the optical gap defined by the "Tauc" linear extrapolation of $(\varepsilon_2 E^2)^{1/2}$ or almost equivalently, $(\alpha E)^{1/2}$, to zero. A basic assumption of the present work is that films, whose thickness (D) ranges from 0.03 to 5μ, are identical, although surface regions (substrate or free) may play a dominant role in certain regions of E, D space.

FILM PREPARATION

The SiH_x films were prepared by glow discharge decomposition of silane (SiH_4) in a capacitive reactor operated at 13.66 Mhz. The discharge electrodes were parallel plates, 6 or 8 inches in diameter, spaced 2 inches apart. The substrates were placed on the lower electrode (anode) which was grounded electrically and heated by a resistance heater. The temperature of the substrates was determined by calibration with a thermocouple embedded in a dummy substrate. Undiluted CVD silane was injected into the reactor through a mass flow controller. The system was pumped by a turbomolecular pump and pressure in the reactor was maintained at 30 mtorr by an adjustable throttle valve. A mass spectrometer and capacitance manometer were used to measure the partial pressure of SiH_4 rich plasma. Low RF power and high SiH_4 inlet rate resulted in a SiH_4 rich plasma; low flow rate and high RF power resulted in a SiH_4 depleted plasma.

For optical measurements, films were deposited on quartz substrates; films for IR measurements were made on optically polished c-Si substrates.

OPTICAL ANALYSIS

In the absence of multiple reflections ($E > E_G$) we analyzed the transmission and free surface reflection coefficient by

$$T_0 = (C\,16\,n_s|\tilde{n}|^2 A)/(|1+\tilde{n}|^2|n_s+\tilde{n}|^2);\; R_0 = |\tilde{n}-1|^2/|\tilde{n}+1|^2. \quad (1)$$

In the above expressions, n_s is the real index of the substrate; C is a coefficient to account for the multiple incoherent reflections in the substrate (for quartz, C = 0.97); $\tilde{n}$ is the complex index of a-SiH_x and A = exp ($-\alpha D$) where D is the film thickness. Reflectivity was measured in non-polarized light at an incidence angle of less than 20°. The c-Si specimen was calibrated at NBS. Iteration of T_0 and R_0 determined $\tilde{n}$ and hence $\tilde{\varepsilon}$.

In the low energy regime, we chose to average adjacent fringes to obtain the incoherent form for the transmission, $\langle T\rangle$:

$$\langle T\rangle = (T_{max}\,T_{min})^{1/2} = T_0/[1-(r_{21}r_{23}A)^2], \quad (2)$$

where $r_{21} = (n-1)/(n+1)$ and $r_{23} = (n-n_s)/(n+n_s)$. In this regime, we neglect the imaginary part of $\tilde{n}$ in r_{21} and r_{23}. We obtain a measurement of n by the magnitude of the transmission minima. These values joined smoothly to those determined by R_0 for $E > E_g$.

The thickness of our films was determined both by contact measurements of a "step" or by analysis of the fringes. The two approaches agreed to about ± 5%.

Both the transmission and photoconductivity measure an average attenuation and cannot, by themselves, distinguish inhomogeneous absorption from homogeneous. To separate surface effects requires films of the same properties, but different thicknesses. For E > 1.75 eV, we believe volume absorption dominates. For 1.60 < E < 1.75, there is some evidence for surface absorption in our films. The "absorption" coefficient in this case is denoted by $\langle\alpha D\rangle/D$.

EXPERIMENTAL RESULTS $E > E_G$

In Fig. 1 we exhibit α and n for anodic films of normal composition $SiH_{0.16}$ prepared at substrate temperatures of 240°C. We ascribe the scatter in α to thickness uncertanty. Fig. 2 displays the data in a form suggested by the Tauc model for optical absorption in a disordered material, with a free electron density of states in both the occupied and unoccupied levels[5]:

$$(\varepsilon_2 E^2)^{1/2} = (E-E_G)\,(e^2 m/2\pi\hbar^2)^{1/2}\,(V\,Da^2)^{1/2} \qquad (3)$$

In the above, E_G is the optical gap, V is the volume of the specimen and Da^2 is the square of the gradient matrix element for the optical transition at energy E. Utilizing $\varepsilon_2 = 2n\kappa$ the above expression is equivalent to $(\alpha E)^{1/2} \approx (E-E_G)$ if n(E) does not vary appreciably in energy.

Following Tauc[5] and Davis and Mott[6]: $VDa^2 = (Vo/V)(VD_x^2) = VoD_x^2$ where D_x is the matrix element equivalent to Da for the direct transition in the crystal. Vo is the "coherence volume" in the disordered solid, i.e. that volume over which sufficient order exists to define momentum.

From Fig. 2 and a value for D_x for c-Si (E > 3.2 eV) we obtain for E > 2.2, Vo $\approx$ $(23A)^3$ and E_G = 1.84 eV. For 1.75 < E < 2.2, Vo $\approx$ $(16A)^3$ and E_G = 1.72 eV. The solid curves in Fig. 1 correspond to Eq. (3) and these parameters.

The striking linear variation for $(\varepsilon_2 E^2)^{1/2}$ over a wide range of E(1.5 eV) is also exhibited for a-Ge[7] and a-Si[8], but with about one half the coherence volume. For a-Si, E_G = 1.5 eV, the Vo for a-$SiH_{0.16}$ corresponds to about 600 atoms. It is interesting to note a recent calculation of Ching and Lin[9] on a 54 atom continuous random network which exhibits good agreement with Eq. (3) above 2.4 eV for $E_G \approx$ 1.5 eV and Vo $\approx$ 1/2 $(23A)^3$. The extended agreement with Eq. (3) appears to be a property of "ideal" amorphous materials both in theory and experiment.

E_G is a "one-parameter" characteristic of the optical properties of the film for E > E_G and is denoted the optical gap. In Fig. 3 we exhibit this quantity as a function of measurement temperature for one film (a-$SiH_{0.24}$). In Fig. 3 we also show the temperature dependence of the indirect gap of c-Si scaled by the ratio of optical gaps at 300°K.[10] The Eo_3 data of Freeman and Paul for sputtered films appears to vary slightly more linearly with temperature than the glow discharge material but has a similar temperature derivative at 300K.[11]

We continue to focus on E_G and in Fig. 4 exhibit its dependence on the temperature of the film during growth. For comparison we exhibit a curve given by the RCA group[12] as well as E_G for an anodic film prepared by Tsai and Fritzche.[2] The agreement is satisfactory.

In Fig. 5 we show E_G as a function of hydrogen concentration where the comparison is again to the work of Tsai and Fritzche[2] as well as Janai et. al.[13] (silane pyrolysis). Where we have not measured the hydrogen directly we have utilized the calibration plot shown in Fig. 5 between the optical density at the Si-H stretch and the measured hydrogen concentration. In Fig. 5 the notation S (small), L (large), and VL (very large) refers to the "dihydride" component in the stretch absorption line.

EXPERIMENTAL RESULTS E $\lesssim$ E_G

In order to continue the optical measurements to regions well below E_G, we have made photoconductivity measurements. We utilize the following relation for weakly adsorbed light: $F\langle\alpha D\rangle \approx I^{1/\gamma}$ where I is the photocurrent, F is the incident flux and γ is a measure of recombination kinetics. γ has the value of 0.7 independent of E in this range. The photoconductivity data was scaled to the optical absorption at 1.8 eV. Fig. 6 shows the results.

There are several noteworthy features of Fig. 6. One is the exponential drop in optical absorption, over two orders of magnitude in 0.25 eV, which has a minimum in the vicinity of a photon energy of 1.5 eV. This is the first experimental evidence for an exponential tail in a-SiH_x.[2] The excitation energy ($\approx$ 0.06 eV) is surprisingly close to that observed for other amorphous materials.[5]

The other noteworthy point is the maximum at 1.3 eV which may be ascribed to structure in the gap states within 0.5 eV of the valence band edge.

SUMMARY

We have shown that the optical properties of a-$SiH_{0.16}$ exhibit reproducible and almost idealized behavior. The absorption edge is a sharp exponential between 1.5 eV and 1.8 eV and is parabolic from 1.8 eV to 4.1 eV. Below 1.5 eV there is evidence for an absorption to a photoconducting state down to at least 1.2 eV, with a maximum at 1.3 eV.

The optical gap defined by Tauc is 1.84 with a coherence volume of 600 atoms. The energy dependence of $(\alpha E)^{1/2}$ can be associated with a reduction of the coherence volume by a factor of two between 1.84 and 1.72 eV for $SiH_{0.16}$.

The optical gap is a convenient and well-defined parameter for measurements at different temperatures or to characterize films prepared under different conditions. The temperature dependence of E_G can be scaled to the temperature dependence of the indirect gap of c-Si E_{ind}, by just the ratio of E_G to E_{ind} (1.63).

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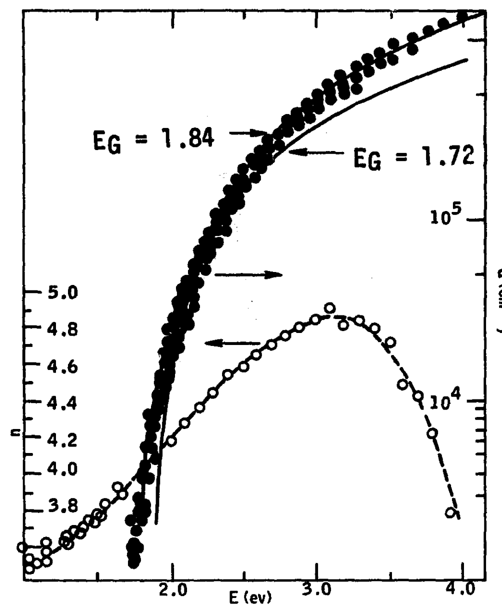

Fig. 1 Attenuation constant α and index n for RFGD films with composition a-$SiH_{0.16}$. The solid curves derive from the low and high energy approximations shown in Fig. 2 for $(\alpha E)^{1/2}$.

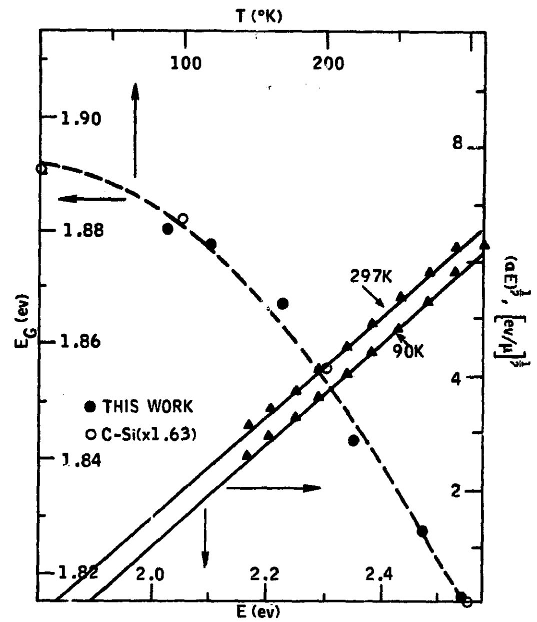

Fig. 3 $E_G(T)$ compared with the indirect gap of c-Si scaled by a factor of 1.63. $(\alpha E)^{1/2}$ as a function of E is shown at 90K and 297K.

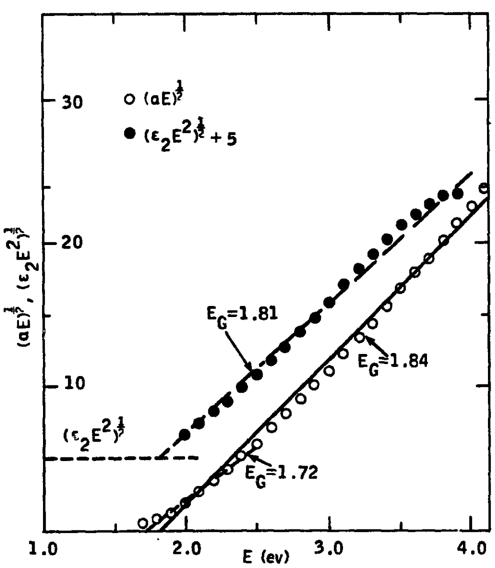

Fig. 2 $(\alpha E)^{1/2}$ and $(\varepsilon_2 E^2)^{1/2}$ from Fig. 1 as a function of photon energy.

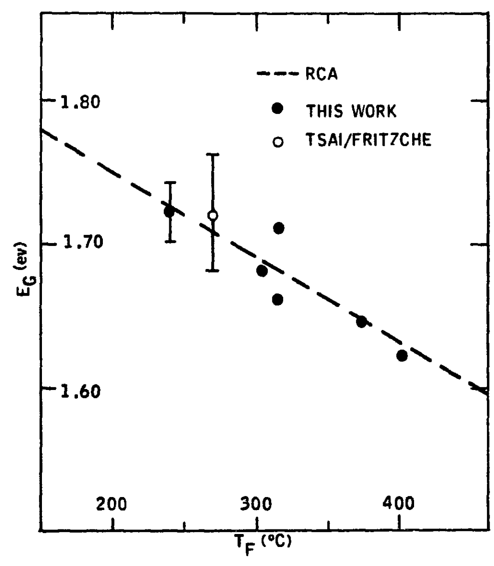

Fig. 4 E_G as a function of substrate temperature, T_F, for anodic RFGD films.

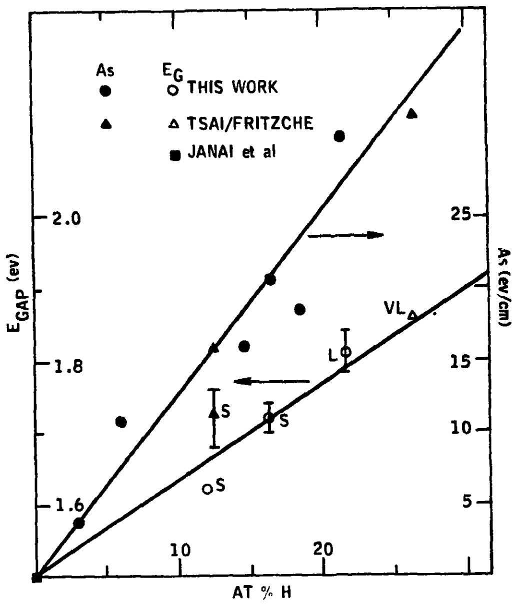

Fig. 5 E_G and integrated absorption at 2000 cm^{-1} (As: Si-H stretch) as a function of at % H. The notation S, L and VL refers to "dihydride" content.

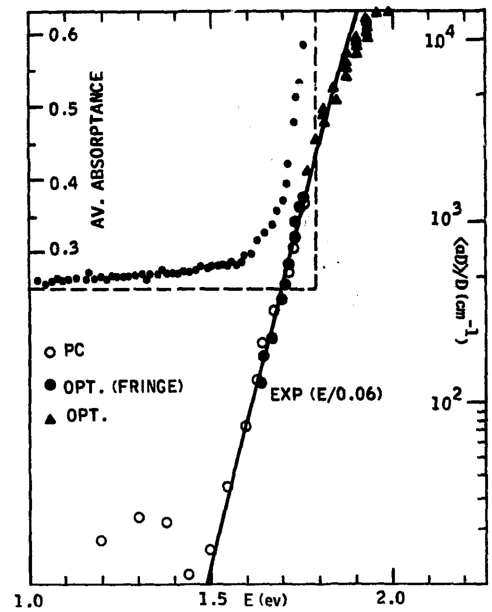

Fig. 6 Comparison of optical absorption inferred from photoconductivity (PC) and derived from optical transmission in fringe region (average absorptance) and in non-fringe region (Fig. 1).

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