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Physics Department, University of Aston, Birmingham[1])

Dependence of the Electronic and Optical Properties of Unhydrogenated a-Si on Preparation Conditions

By

S. A. Abo-Namous[2]), Y. Zaka, and R. W. Fane

The optical and electronic properties of undoped a-Si are studied over a wide range of preparation conditions. The results indicate that the conductivity, photoconductivity, optical gap, and the position of the Fermi level in the gap can be controlled by varying the product (Pd/U_{sb}); P, d, and V_{sb} are the gas pressure, the target-substrate distance, and the self-bias voltage on the target, respectively. This is attributed to controlling the density-of-states distribution in the gap.

Die optischen und elektronischen Eigenschaften von undotierterem a-Si werden für einen großen Bereich der Präparationsbedingungen untersucht. Die Ergebnisse zeigen, daß die Leitfähigkeit, Photoleitfähigkeit, optische Bandlücke und die Lage des Ferminiveaus in der Bandlücke durch Variation des Produkts (Pd/V_{sb}) gesteuert werden können; P, d und V_{sb} bedeuten dabei den Gasdruck, den Abstand Target–Substrat bzw. die Eigenvorspannung des Targets. Das wird der Steuerung der Zustandsdichteverteilung im Gap zugeordnet.

1. Introduction

Over the last decade the techniques for producing hydrogenated amorphous silicon (a-Si:H) have become well established [1, 2]. Although a-Si:H has some useful and interesting properties, there seems to be uncertainty about its thermal stability [3] and the role of hydrogen [4]. In recent years attempts have been made to produce a-Si, without hydrogen, which has properties comparable with those of a-Si:H. The resistivity of a-Si produced by rf sputtering in pure argon has been increased from 10^3 to 10^8 Ωcm by increasing the argon gas pressure or the target–substrate distance [5], but the films were found to be porous and susceptible to oxygen contamination. Attempts to change the electrical properties by substitutional doping were only moderately successful. Amorphous silicon produced by magnetron sputtering in argon has also shown promising results.

In this laboratory we have produced a-Si with room temperature resistivity of the order of 10^8 Ωcm by rf sputtering in high pressure neon [6], and recently n- and p-type doping by co-sputtering from composite targets [7, 8] has shown doping efficiencies comparable with other techniques.

In an attempt to understand how the preparation conditions affect the quality of the films produced, we have studied the optical and electronic properties of a-Si films over a wide range of preparation conditions. In this communication we report the effect of varying the neon gas pressure between 40 and 220 mTorr, the substrate–target distance between 2 and 5.3 cm, and the rf self-bias on the target from 650 to 1000 V.

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[1]) Gosta Green, Birmingham B4 7ET, Great Britain.

[2]) Permanent address: Material Science Department, Kuwait Institute for Scientific Research, Kuwait.

2. Sample Preparation

The amorphous silicon was deposited in a radio-frequency diode sputtering system, with a water cooled target holder and substrate holder in a plane-parallel arrangement with a rotatable shutter between them. The target was a single crystal wafer of electronic grade silicon. The substrate can be electrically heated up to 500 °C, but for the present experiments all the films were deposited at around 300 °C. A Helmholtz pair of coils gives a field of about 0.01 T at the centre of the discharge. The base pressure in the sputtering chamber was of the order of 10^{-7} Torr achieved by an oil diffusion pump with a baffle and a liquid nitrogen cooled trap. Corning 7059 glass substrates were ultrasonically cleaned in a detergent, rinsed in distilled water, and then boiled in isopropyl alcohol before placing in the chamber.

Neon gas (99.999%) was admitted into the chamber via a needle valve, thus by controlling the flow rate the desired pressure can be attained. The target–substrate separation was varied from 2 to 5.3 cm.

The composition of the films was analysed by X-ray photoemission. The neon incorporated into the film was below the detection limit of this technique. Also the presence of surface plasmons and the absence of chemical shifts in the photoemission spectra are indicative of oxide free films.

3. Measurements and Results

The film thickness was measured using a multiple-beam interferometer with an estimated uncertainty of $\pm 10\%$. The film thickness ranged from 0.3 to 1.5 μm. The deposition rate D_R of the films was measured as a function of the ratio (Pd/U_{sb}) of the sputtering gas pressure (P), the target–substrate separation (d), and the rf self-bias voltage (U_{sb}). This is shown in Fig. 1. It can be seen from this figure that D_R varies exponentially from about 4 Å/s for low Pd/U_{sb} to $\lessapprox 1$ Å/s for high Pd/U_{sb}. This type of variation seems to be consistent with the fact that the number of silicon atoms which reach the substrate without suffering collisions would be expected to be proportional to the exponent of $-Pd$. The very slow variation in D_R at higher Pd/U_{sb} products would also logically follow from this.

The dc dark conductivity was measured using gap-cell configurations with Al electrodes separated by 1 mm. A Keithley 610C electrometer was used for the measurements with an applied field of about 10^2 Vcm^{-1}. Al electrodes proved to make good ohmic contacts with a-Si within the range of applied field used. The room temperature conductivity, σ_{RT}, can be varied systematically over more than four orders of magnitude from $\approx 10^{-5}$ to less than 10^{-9} Ω^{-1} cm^{-1} by varying the product Pd/U_{sb} (Fig. 2).

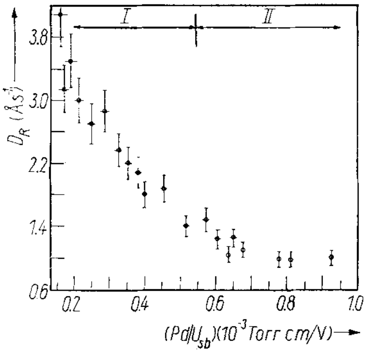

Fig. 1. The deposition rate D_R as a function of Pd/U_{sb}. P, d, and U_{sb} are gas pressure, target–substrate separation, and self-bias voltage, respectively

Although this effect has been observed in Ar sputtering [9] the final conductivity attained by Ne sputtering is two to three orders of magnitude lower than that produced by Ar sputtering.

The dark conductivity of the films was measured as a function of temperature, and the thermal activation energy ΔE_a was deduced from the $\lg \sigma$ versus $1/T$ plots. Fig. 2 also shows the change in ΔE_a with Pd/U_{sb}; which is seen to change in a manner consistent with the variation in σ_{RT}, and approaches a steady value of nearly 0.85 eV. This value is comparable with those values using glow-discharge and Ar/H_2 sputtering techniques.

The conduction type of these intrinsic films was readily determined from the polarity of the room temperature thermopower sign observed by the hot-probe technique. All the amorphous samples reported here were n-type.

The optical gap E_0 was determined from the plots of $(a\hbar\omega)^{1/2}$ versus $\hbar\omega$ according to the relation [10, 11]

$$(\alpha\hbar\omega)^{1/2} = B(\hbar\omega - E_0)\,. \tag{1}$$

B is a constant, $\hbar\omega$ the photon energy, and α the absorption coefficient calculated from the transmission data, assuming a reflection coefficient independent of wavelength at long wavelengths. The dependence of E_0 on Pd/U_{sb} is shown in Fig. 2. The optical gap increases from about 1.4 eV at low values of Pd/U_{sb} to about 1.85 eV at higher Pd/U_{sb}.

The absorption coefficient α is plotted against $\hbar\omega$ for a few samples with different Pd/U_{sb} products (Fig. 3). The lower values of α were determined by normalizing the photoconductivity data at low energies using the method of Moddel et al. [12]. It is apparent from Fig. 3 that upon increasing the value of Pd/U_{sb} the density of gap states due to bonding defects is reduced. The data presented in this figure are compar-

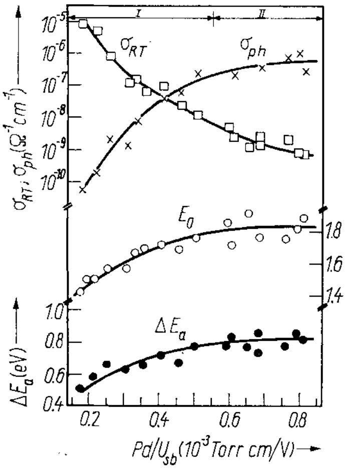

Fig. 2

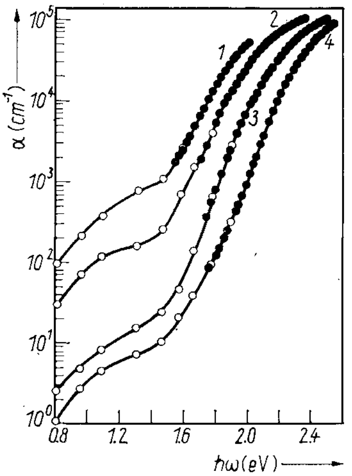

Fig. 3

Fig. 2. The room temperature conductivity σ_{RT}, the photoconductivity σ_{ph}, the thermal activation energy ΔE_a ,and the optical gap E_0 as functions of Pd/U_{sb}

Fig. 3. The absorption coefficient α vs. photon energy $\hbar\omega$ for different values of Pd/U_{sb}. (1) 0.31, (2) 0.46, (3) 0.61, and (4) 0.79 mTorr cm/V. The open circles are the normalized photoconductivity using Harvard group's method [12]

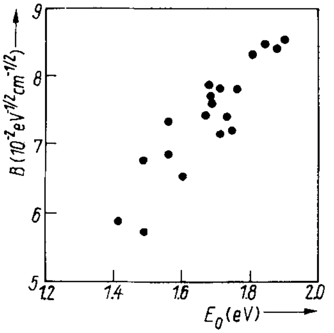

Fig. 4. The slope B of the plot $(\alpha\hbar\omega)^{1/2}$ vs. $\hbar\omega$ against the optical gap E_0

able to the results for a-Si:H obtained elsewhere [13]. Also the variation in the constant B in the above equation with the optical gap E_0 (Fig. 4) is further support for the above conclusion.

The shift of the absorption curve of Fig. 3 to higher energies with increased Pd/U_{sb} product is similar to the shift found for a-Si:H films upon increasing H_2 content [14].

The variation in the optical properties with Pd/U_{sb} is consistent with the variation of both the electrical conductivity and thermal activation energy mentioned earlier.

It is interesting to note that the absorption at lower energies ($<$ 1.5 eV) is reduced upon increasing Pd/U_{sb}. This implies a reduction in the localized-defect-states density comparable to results found for glow-discharge and Ar/H_2 sputtered material.

The photoconductive experiments were carried out using the same gap-cell configuration as for the dark conductivity measurements. The steady photocurrent was measured for an applied field of about 10^2 Vcm^{-1}. The films were illuminated by a monochromatic light with energy 1.89 eV and $\leqq 10^{15}$ photon/cm^{2}s flux intensity. The room temperature photoconductivity σ_{ph} is shown as a function of $Pd/_{sb}U$ product in Fig. 2. It can be seen from this figure that σ_{ph} increases rapidly as Pd/U_{sb} is increased. A steady value of $\gtrapprox 10^{-6}\ \Omega^{-1}\ cm^{-1}$ compares well with the photoconductivity of a-Si:H [15, 16]. It can be concluded from Fig. 2 that σ_{ph} increases with ΔE_a in an analogous way to that observed for a-Si:H with low H_2 content (Paul and Anderson [17]). Evidently, increasing Pd/U_{sb} leads to a reduction of the overall density of states in the mobility gap.

4. Discussion and Conclusion

The similarities between the changes in optical and electrical properties and the deposition rate shown in Fig. 1 and 2 imply that the deposition rate (D_R) plays an important role in controlling the properties of the films. Upon increasing Pd/U_{sb}, at a fixed substrate temperature, the decrease in dark conductivity σ_{RT} and the increase in photoconductivity σ_{ph} are consistent with the increase in both the thermal activation energy of the dark conductiivty ΔE_a and the optical gap E_0 (Fig. 2). It is interesting to point out that the increase in σ_{ph} with Pd/U_{sb} of our films is qualitatively similar to the increase of σ_{ph} with hydrogen content in a-Si:H produced at low hydrogen partial pressure by Ar/H_2 sputtering [17]. This has been attributed to reducing the density of states in the mobility gap.

The slow change both in the deposition rate (Fig. 1, range II) and in the optical and electronic properties (Fig. 2, range II) indicates the optimum range of the parameters U_{sb}, P, and d for Ne sputtering. It may be possible, however, to improve further the films by changing some other parameters not examined here. For example negative substrate bias has recently been shown to improve the electronic and optical properties of a-Si [18].

From the plots of α versus $\hbar\omega$ for various films prepared under different conditions (Fig. 3), it can be seen that upon increasing the product Pd/U_{sb} the absorption edge between $\alpha = 10^4$ and 10^5 cm^{-1} is displaced to higher energies. Similar changes have been reported for a-Si:H [13], and were attributed to hydrogen satisfying the dangling bonds and relaxing the a-Si network. The slope B in (1), plotted against the optical gap E_0 in Fig. 4, shows a linear relationship. This is similar to the case for glow-discharge [14] and sputtered [17] a-Si:H. This relation may suggest that the increase in the optical gap is due to reduction of the band tail-states density or gap defect states or both [17], which in turn might lower the overall density of states in the mobility gap. Lowering the shoulder around 1.2 eV in the optical absorption data of Fig. 3 upon increasing the Pd/U_{sb} product is in support of this argument.

The above results demonstrate the control of electronic and optical properties of intrinsic a-Si by the preparation conditions, when sputtering in Ne plasma. Relatively high gas pressure and moderate target–substrate spacings and self-bias voltage can produce films with low density of states in the mobility gap. It can be argued that the deposition rate is controlled both by the kinetic energy of the sputtering gas species, ions and neutral particles, bombarding the target and the subsequent collisions within the gas, which include the Ne–Ne and Si–Ne collisions (both ions and neutrals). In addition the plasma contains energetic electrons that are accelerated across the target plasma sheath [19]; these electrons hit the substrate. Increasing Pd product enhances the collisions within the plasma and hence reduces the kinetic energy of the particles arriving at the substrate surface. Priestland and Jackson [20] estimated that with $P = 10^{-3}$ Torr and $d = 6$ cm, about 60% of the sputtered material will experience collision with the sputtering gas species during transit from the target to the substrate. U_{sb} is also expected to play a role in controlling the kinetic energy of the particles arriving at the substrate surface. Therefore, moderating the kinetic energy of the Ne species and the sputtered Si particles, by the above quantities, will result in less damage in the deposited film in addition to the possibility of re-constructing some weak bonds in the Si network.

Comparison of the influence of the preparation conditions of sputtering in Ne on the film properties with that of sputtering in Ar [9] indicates that Ne produces a material with less defect states. This is consistent with the bigger energy exchange to be expected in the case of Si–Ne collisions compared with Si–Ar collisions.

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