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Composition and properties of unhydrogenated amorphous silicon produced by sputtering in argon or neon gas

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The electrical and optical properties of amorphous silicon produced by rf sputtering in pure argon or neon gas are compared. The effect of varying the inert gas pressure has been investigated. It is shown that the density of defect states can be reduced by sputtering in high pressure neon instead of the conventionally used argon. The composition of the films has been studied by Rutherford backscattering spectroscopy (RBS) and X-ray photoemission spectroscopy (XPS).

Introduction

Inherent in all methods of producing amorphous silicon (a-Si) films is the presence of large numbers of dangling bonds and microvoids. These defects introduce localized states in the mobility gap between the conduction and valence bands, thus hindering the control of electrical properties by substitutional doping[1]. Hence a large fraction of research has been directed towards reducing the density of defects to a sufficiently low level to allow efficient doping.

In 1975 Spear *et al*[2] were the first to dope a-Si produced by the glow-discharge decomposition of SiH_4 with phosphorous and boron. Their method succeeded because the hydrogen present in the plasma attached itself to the dangling bonds thus reducing the density of states in the gap. Soon after, a-Si produced by rf sputtering in Ar/H_2 plasma was also doped successfully[3]. The success with doping a-Si:H alloy and the realization of its potential device capabilities have diverted a lot of attention away from the need to investigate the basic parameters affecting film properties and to optimize them to achieve 'pure' a-Si films with a low density-of-defect-states. Instead experimentalists have saturated the silicon with dangling-bond terminators such as hydrogen or the halogens to achieve the desired properties. Concentration of these intentionally incorporated impurities can be as large as 26%[4]. Compensation by hydrogen may remove the gap states, but the interaction of nearby Si–H units may reintroduce gap states near the conduction band[5]. The long term stability of these films is questionable since hydrogen effuses at 350°C and there is some evidence that hydrogen effuses even at room temperature[6].

It is therefore important to optimize the preparation conditions to give pure a-Si films with a low density-of-defect-states. In this paper we report the effects of varying the sputtering gas and pressure on the composition and electrical and optical properties of a-Si films produced by rf sputtering in (99.999%) pure argon and neon gases. The films produced have been characterized by measuring the electrical conductivity over a temperature range of 200°C. The optical gap has been determined by transmission measurements in an UV-Vis spectrophotometer. Compositional analysis has been carried out by Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS). In particular, the amount of rare gas incorporated into the silicon matrix as a function of gas pressure was investigated. Problems related to the determination of the density of the films from the RBS spectra are also discussed.

Experimental details

Experimental details have been described elsewhere[7]. Briefly, the apparatus consists of a diffusion pumped, rf diode sputtering arrangement with a baffle and liquid nitrogen cooled trap. A Helmholtz pair of coils gives a field of about 0.01 T at the centre of the discharge. The power input is adjusted to give an rf self bias on the target of about 900 V. The target-substrate distance is set at 3.5 cm and the substrate temperature maintained at approximately 200°C, measured with a chromel–alumel thermocouple. Films were deposited simultaneously on several substrates. Corning 7059 glass was used for electrical and optical measurements; for RBS measurements, carbon, crystalline silicon, alumina and quartz substrates were used while aluminium substrates were used for XPS measurements. The rare gases entered the chamber via a needle valve which controlled the flow rate to achieve the desired pressure.

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Film thickness, measured by a multiple-beam interferometer, ranged from about 200 to 1000 nm. Deposition rate varied from about 0.2 nm s^{-1} for high pressure argon films to about 0.4 nm s^{-1} for low pressure films, for neon-sputtered films the deposition rate decreased from about 0.3 to 0.1 nm s^{-1} on increasing the sputtering pressure.

Electrical and optical properties

The electrical conductivity of the films was measured in the manner described elsewhere[7]. Figure 1 shows the variation of room-temperature electrical conductivity, σ_{RT}, with sputtering pressure for argon and neon gases. It is seen that by increasing the argon pressure from 0.67 Pa to about 5.3 Pa, σ_{RT} decreases by more than five orders of magnitude, any further increase in pressure has little effect on σ_{RT} other than increasing it slightly at the higher pressures. The highest pressure at which we can operate with argon is limited by the geometry of the system and is about 14.6 Pa beyond which the mean free path of the argon ions becomes comparable to the spacing between the target and the earthed shield surrounding it. For neon this limitation is not so severe and sputtering pressures up to 40 Pa can be tolerated. For neon, an increase in the pressure from 0.67 to 5.3 Pa had a similar

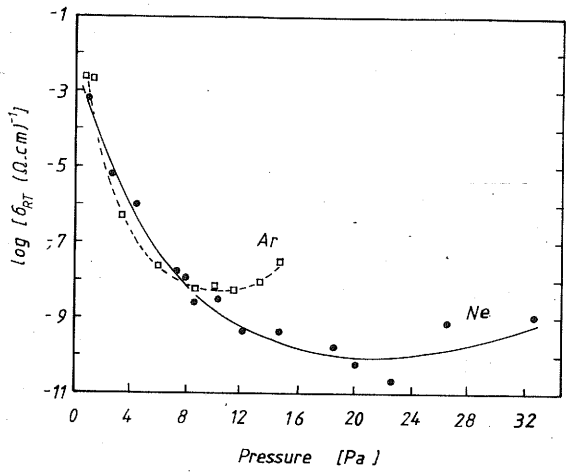

Figure 1. The room-temperature conductivity, σ_{RT}, as a function of sputtering pressure.

effect but an increase in the pressure to about 20 Pa further decreased the conductivity by more than three orders of magnitude. Any further increase in pressure again, as in the case of argon, produced a reversal in the trend with the conductivity increasing with pressure.

A similar behaviour is observed in the variation of thermal activation energy, ΔE, and the optical gap, E_o, with pressure as illustrated in Figure 2. For argon ΔE increases from 0.14 eV to about 0.6 eV as the pressure is increased from 0.67 to 8.6 Pa and any further increase in pressure has little effect. For neon, ΔE increases with pressure to a value of about 0.9 eV at 14.6 Pa, higher pressure results in a slight decrease in ΔE. The optical gap was determined from the plots of $(\alpha\hbar\omega)^{1/2}$ vs $\hbar\omega$ according to the relation[8].

$$(\alpha\hbar\omega)^{1/2} = \beta(\hbar\omega - E_o)$$

where β is a constant, $\hbar\omega$ the photon energy and α the absorption

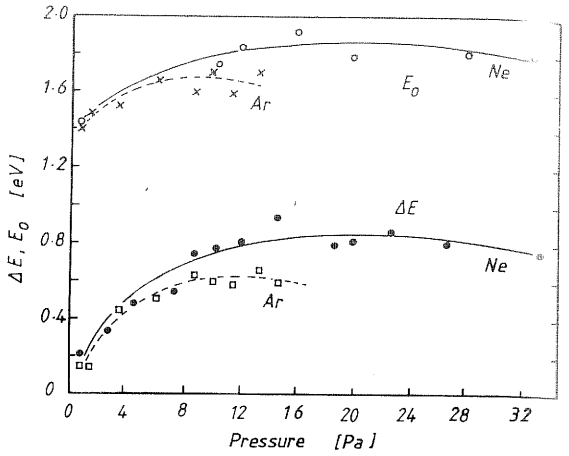

Figure 2. The variation of thermal activation energy. ΔE, and the optical gap, E_o, with sputtering pressure.

coefficient. The optical gap, E_o, increases from about 1.4 eV at low pressure to about 1.7 eV for high-pressure sputtering in argon and 1.8 eV for the neon case.

Compositional analysis

Figure 3 shows the ratio of argon and neon atoms to silicon atoms in the films as a function of sputtering pressure. Rutherford backscattering spectroscopy using 2.8 MeV He ions and XPS using Mg Kα radiation were used to determine the argon and neon contents of the films respectively. The ratio of argon to silicon atoms of the films was found to decrease from about 6.0% at low pressure to less than 0.5% for high pressure. The variation of neon in the films with pressure exhibits a similar trend to that of argon; however, at any given sputtering pressure the neon incorporated in the films is approximately twice as much as argon. Inspection of RBS spectra readily confirmed that the argon was distributed uniformly throughout the films; however, to verify the uniformity of neon in the silicon matrix, films had to be etched by argon bombardment and spectra taken at various depths.

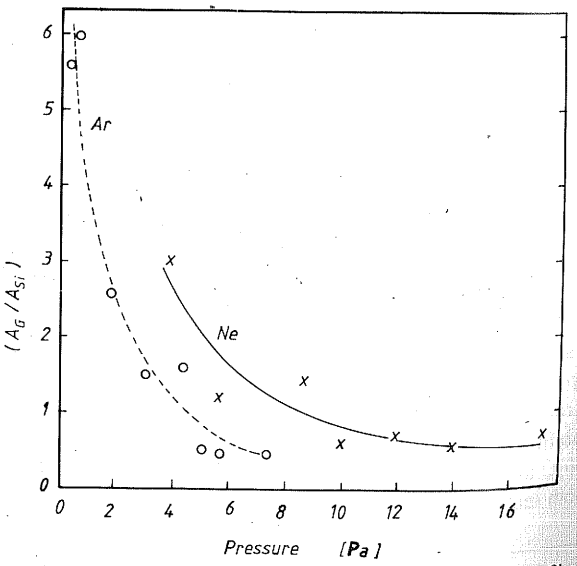

Figure 3. The ratio of argon and neon atoms to silicon atoms in the film as a function of sputtering pressure.

Discussion and conclusions

The results indicate that the density of defect states in a-Si can be reduced by sputtering at high pressures. For sputtering in pure argon this is evidenced by a decrease in room-temperature electrical conductivity by more than five orders of magnitude and an increase in the thermal activation energy from 0.14 to 0.6 eV as the argon pressure is increased from the conventionally used value of 0.67 Pa to 8.7 Pa.

Similar results on argon sputtering have been reported by others. Pawlewicz[9] decreased σ_{RT} from about 10^{-3} to about 10^{-7} $(\Omega\,\mathrm{cm})^{-1}$ by increasing the argon gas pressure from 3.3 to 20 Pa and there was corresponding increase in the activation energy from 0.2 to 0.3 eV. Van Dong *et al*[10] sputtered in a dc triode system and obtained, under a special condition of heating, a-Si films with $\sigma_{RT} < 10^{-9}$ $(\Omega\,\mathrm{cm})^{-1}$ and activation energy of about 0.8 eV. Shimizu *et al*[11] decreased the electrical conductivity by more than five orders of magnitude by increasing the product of argon pressure, P, and target–substrate spacing, d, from 13 to 130 Pa-cm. The original suggestion by Pawlewicz[9], that increasing the sputtering pressure reduced the kinetic energy of the various species bombarding the film thus reducing the number of defects, seems to be consistent with the above results. However, recently it has been found that the low conductivity of the high pressure argon-sputtered films could be due in part to post-deposition oxidation because the films have a porous structure[12]. This is thought to be due to the fact that although bombardment by high energy species (ions, neutrals, electrons) in the plasma is detrimental to the film properties, some bombardment is beneficial in that it helps to remove loosely bound atoms. Thus a film grown under the condition of high pressure, where the plasma species have become thermalized before reaching the substrate; tends to have a porous structure.

To investigate this hypothesis, the oxygen content of the films was extracted from the relevant RBS spectra. The results are summarized in Figure 4. From these results it is evident that films produced in argon sputtering pressures up to 3.5 Pa are essentially oxygen free, while films produced at higher pressures contain about 20% oxygen.

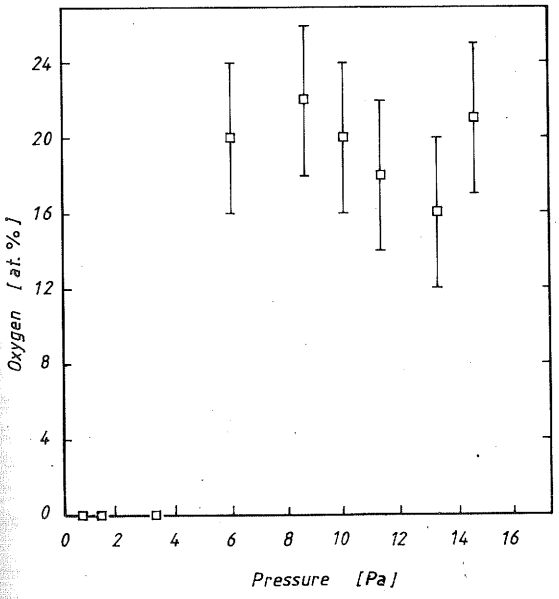

Figure 4. Concentration of oxygen in argon-sputtered films as a function of sputtering pressure.

Our results appear to support the suggestion that as the gas pressure is increased the electronic and optical properties of the films improve due to the reduction in the kinetic energy of the various species in the plasma which are continuously bombarding the growing film. This is evident from a decrease in σ_{RT} by four orders of magnitude as the pressure is increased from 0.67 to 3.5 Pa, while maintaining essentially oxygen free films. The variations of thermal activation energy, optical gap and the argon content with argon pressure have a similar relationship; ΔE and E_0 increase and the argon content decreases sharply as the pressure is increased from 0.67 to 3.5 Pa. Increasing the pressure beyond 3.5 Pa also removes low energy bombardment of the film which is beneficial in that it removes loosely bound material from the surface of the films, thus films produced at high argon pressure tend to be porous and susceptible to post-deposition oxidation as is evident by a sharp increase in the oxygen content of the films produced at pressure higher than 3.5 Pa. The decrease in σ_{RT} as the pressure is increased beyond 3.5 Pa is less sharp, levelling off at pressures of about 8.6 Pa and is probably due to the oxygenation of the films. Similarly ΔE and E_o increase and the argon content decreases slightly as pressure is increased beyond 3.5 Pa and eventually levels off at about 8.6 Pa.

Another quantity which can be used to support the above argument is the measurement of the density of the films. This could in theory be readily obtained from the RBS spectra and the thickness of the film, measured independently by other means, employing the relation[13]

$$\Delta\varepsilon = [\theta]\frac{N_0\rho}{A}t$$

where $\Delta\varepsilon$ is the energy difference between the energy of the ions scattered from the front surface of the target and the ions scattered from the back surface of the target, $[\theta]$ is the stopping cross-section, N_0 is Avogadro's number, A is the atomic weight of element and ρ and t are the density and thickness of the film respectively. Since $[\theta]$ is tabulated[14] the density can be obtained by measuring $\Delta\varepsilon$ and the thickness of the film. We attempted to measure the density by depositing the films on carbon substrates since the carbon edge lies well below the silicon peak, but measurement of $\Delta\varepsilon$ and the shape of the peak indicated that carbon and silicon had diffused into each other, resulting in the broadening of $\Delta\varepsilon$, and hence an over-estimation of the density. To overcome this problem, quartz and alumina substrates were employed and although no sign of diffusion seemed apparent, there was a large error in determining $\Delta\varepsilon$ due to the overlap of the silicon and the substrate peaks. Thus, so far we have been unable to measure the density of the films but further work to overcome the problems indicated above and to investigate alternative methods is in progress.

It can be seen by inspection of Figures 1–3 that the variations in properties of neon-sputtered films follow the same general trend as for argon. However, in this case the region of rapid changes in properties with increase in pressure extends up to 12 Pa. An increase in pressure from 0.67 to 12 Pa results in a decrease in σ_{RT} by more than six orders of magnitude to less than 10^{-9} $(\Omega\,\mathrm{cm})^{-1}$, accompanied by an increase in ΔE and E_o by 0.6 eV and 0.4 eV respectively. The neon concentration in these films decreases to about 1.0 at .% at 12 Pa and levels off at about 0.5 at .% at higher pressures.

The pressure region 0.67–12 Pa for neon corresponds to the region 0.67–3.5 Pa for argon, in that the improvement in film properties is believed to result from the thermalization of plasma species. However it is apparent from the results that improvement of film quality is greater for neon-sputtered films. Further increase in pressure leads to contamination by oxygen, although figures for oxygen content have only been obtained for argon-sputtered films.

Detailed examination of the sputtering plasma is required to determine the factors which result in an improvement in film quality when using neon as opposed to argon sputtering. Thermalization as mentioned above, is important but this may be achieved in either case by using the appropriate pressure. Other factors may be important. The higher ionization potential for neon means that there is less likelihood of doubly charged ions which would result in greater damage to the film. For a given energy the smaller stopping distance for argon ions results in a larger energy dissipation per unit path length and consequently more damage to the growing film. Small atomic size could also be important in causing less structural deformation. There is a higher probability for clusters of atoms to be sputtered with argon[15] which could result in film inhomogeneity and also lead to lower doping efficiency[16].

Finally, the effect of the magnetic field needs to be assessed and, although this feature is again common to both gases used in our system, the effectiveness of this constraint will be different in the two cases.

In summary, the present results indicate that sputtering in high pressure neon can produce a-Si with low density-of-defect-states. Further support for this observation is given by photoconductivity measurements[17] and efficient n- and p-type doping[18,19].

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