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HIGHLY DOPED SPUTTERED AMORPHOUS SILICON WITHOUT HYDROGEN

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A method of producing high resistivity amorphous silicon ($\sim 10^8$ Ω cm) by sputtering without any addition of hydrogen or halogen is described. Such material has been doped n-type using tantalum, to give conductivity values in excess of 1 $(\Omega\ \mathrm{cm})^{-1}$.

1. Introduction

In a previous communication the production of amorphous silicon without the addition of hydrogen was described [1] using a diode sputtering system employing neon in place of the more usual argon as sputtering gas. The effect of the addition of aluminium was also considered. Recently some other attempts to produce α-Si without hydrogen or a halogen have been reported notably by Vandong et al. [2]. A special dc sputtering technique was used and results showed that high resistivity intrinsic material could be produced and conductivities up to about 5×10^{-4} $(\Omega\ \mathrm{cm})^{-1}$ were obtained by suitable doping. High pressure argon sputtering has also been reported [3,4]. Although high intrinsic resistivity was obtained in these films there was some evidence of porosity. The incorporation of aluminium changed the conductivity but the activation energy was always > 0.5eV and was accompanied by a change in the optical gap. This change in band gap was thought to be mainly responsible for the conductivity changes observed.

Theoretically a material with a low density of gap states should be possible. Polk [6] suggested a random network with all bonds satisfied provided small deviations in bond length and angle are allowed. Our early trials coupled with esr measurements indicated that better films could be produced by a method similar to that described here when compared with argon sputtering. Gas content of the film is difficult to determine but preliminary electron-probe results indicate much less neon inclusion in neon sputtered films than argon in the case of argon sputtering. We have no evidence so far that films prepared as described below satisfy such models as that proposed but they have interesting properties, namely a high intrinsic resistivity ($\sim$ 10^8 Ω cm), a thermal

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activation energy of about 0.7 eV and can be made n or p-type. Previously [1] results of the inclusion of aluminium were given and the work has now been extended using tantalum doping to give films with n-type characteristics, some of which have very high conductivity.

2. Experimental details

The apparatus consists of a diffusion pumped rf diode sputtering arrangement with a liquid nitrogen trap. A Helmholtz pair of coils gave a field of about 0.01 T at the centre of the discharge. The target potential is usually measured using a circuit similar to that described by Rock and Smith [6] and Lamont and Turner [7]. The silicon target has a diameter of 7.5 cm and is water cooled. In all cases prior to operation the system was baked and the substrate thoroughly outgassed so that the base pressure was about 5×10^{-7} Torr. The pumping speed is reduced by means of a baffle valve. Neon gas (99.999%) is admitted by a needle valve, the flow rate can thus be adjusted to give the required pressure, generally 200 mTorr. The clean Corning 7059 substrates were protected by a shutter so that clean and stable sputtering conditions could be established before film deposition commenced.

For doping experiments composite targets were used, a piece of tantalum, 0.03–1.80% of the total area being placed on the silicon. So far analysis of the impurity content of the films has not been completed and the figures quoted are for the expected percentage of doping species in the plasma relative to silicon allowing for the sputtering rate [8]. Tantalum was chosen for n-type doping as it is readily available with the required purity and in a form suitable for incorporation into a sputtering target. The temperature of the substrate holder is monitored by a thermocouple during the deposition, and can be maintained at the required temperature by reducing the current to the substrate heater during deposition to offset the heat generated by the plasma. This technique allows the temperature to be varied between 150–400°C. Most of the films were deposited at 300°C. Film thickness, generally 0.5 to 1 μm, was determined by multiple beam interferometry on an edge produced by masking and overlayed with aluminium.

3. Experimental results

3.1. Electrical characteristics

Electrical conductivity measurements were made in vacuum using the gap-cell configuration with nichrome or aluminium deposited immediately after preparation of the film. These contacts were ohmic for the electric field used, generally 10^2 V cm^{-1}. Fig. 1 shows plots of log σ against T^{-1} for a

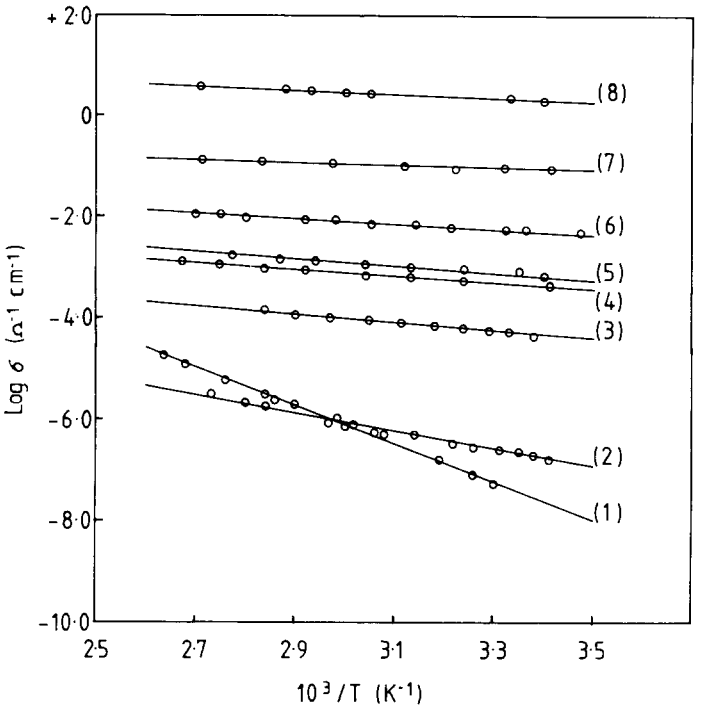

Fig. 1. Log σ against $1/T$ for varying percentages of tantalum in the composite target.

number of intrinsic and n-type films. Table 1 summarises the results including room temperature conductivities (σ_{RT}) and activation energies (ΔE), satisfying the equation

$$\sigma = \sigma_0 \exp(-\Delta E/kT). \tag{1}$$

Films 7 and 8 should be particularly noted as having very high room temperature conductivities and low thermal activation energies.

Table 1
The variation of electrical conductivity at room temperature σ_{RT}, activation energy ΔE and the optical gap E_0 with tantalum concentration

Sample	Impurity conc. Ta (at. %)	Room temperature conductivity (Ω^{-1} cm^{-1})	ΔE (eV)	Optical gap (eV)
(1)	intrinsic	2.5×10^{-8}	0.73	1.64
(2)	0.015	8.0×10^{-8}	0.48	1.64
(3)	0.04	4.5×10^{-5}	0.17	1.52
(4)	0.05	4.3×10^{-4}	0.13	1.52
(5)	0.1	6.6×10^{-4}	0.13	1.52
(6)	0.25	5.0×15^{-3}	0.09	1.41
(7)	0.50	8.0×10^{-2}	0.07	1.41
(8)	0.90	2.0	0.08	1.33

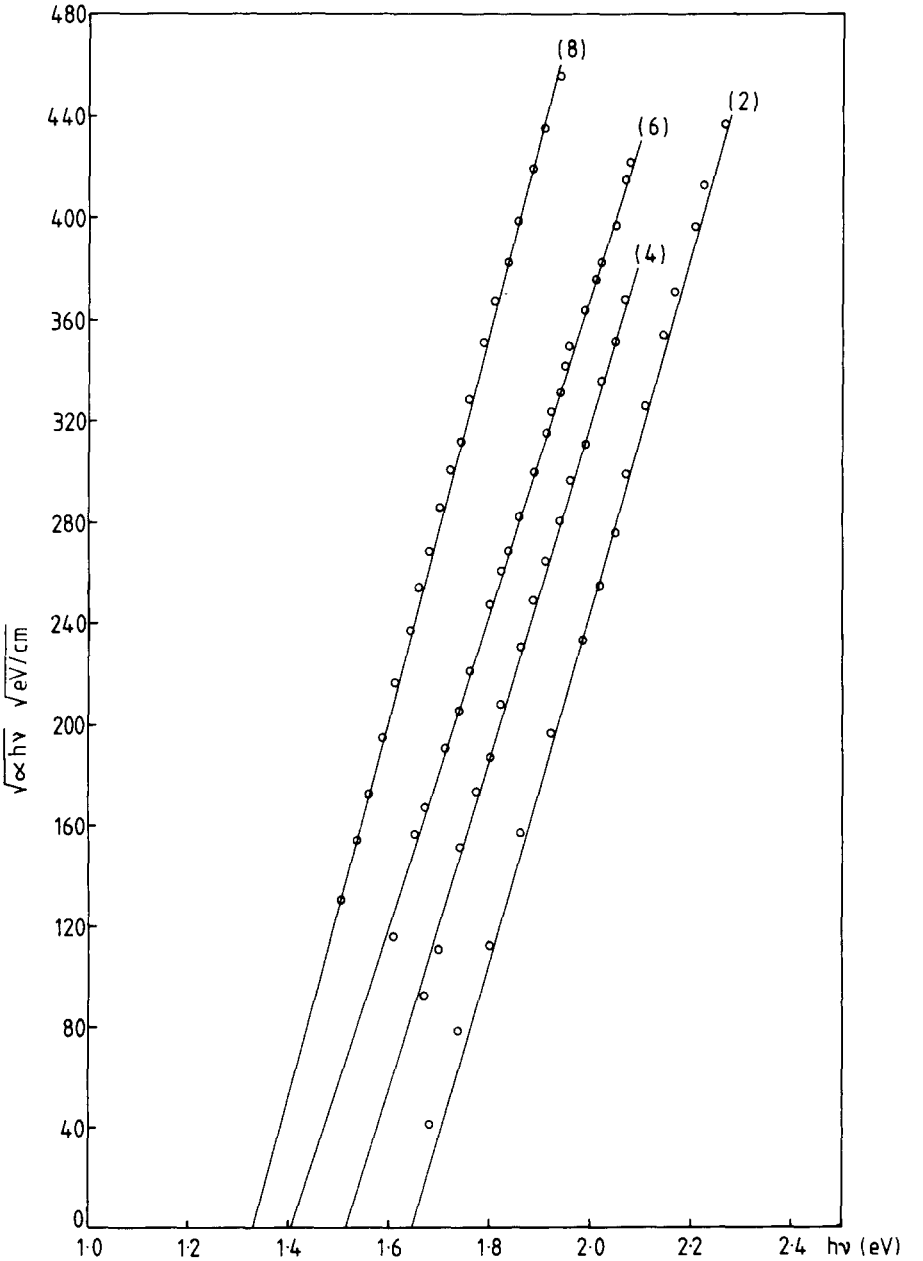

Fig. 2. $(\alpha h\nu)^{1/2}$ versus $h\nu$ for samples deposited from composite targets with 0.015–0.90 at % tantulum. For clarity only samples 2(0.015 at. % Ta), 4(0.05 at. % Ta), 6(0.25 at. % Ta) and 8(0.90 at. % Ta) are included.

3.2. Optical gap measurements

Fig. 2 shows the absorption data for some of the samples determined by means of an optical spectrophotometer. The data has been plotted in the usual way as $(\alpha h\nu)^{1/2}$ against photon energy, $h\nu$, where α is the absorption coefficient, on the assumption of constant matrix elements for electron transitions and a parabolic density of states. Good straight lines were obtained resulting in the optical gaps as summarised in table 1.

4. Discussion

It has been demonstrated that the material, produced as described above, can be doped n or p-type [1]. Confirmation of the type of doping has been by thermoelectric measurements. In addition heterojunctions have been made from the deposition of tantalum-doped α-Si on to crystalline p-type silicon. Satisfactory rectification was observed (fig. 3). The results are comparable with those of Thompson et al. [9]. The same construction but based on n-type crystalline silicon showed no rectifying characteristic.

It will be seen that while the conductivity can be changed over many orders of magnitude and the Fermi level moved by more than 0.6 eV the optical gap only changes from 1.66 eV to 1.33 eV in the extreme cases. Consequently we believe the material has been doped in the accepted manner rather than being modified to a different material as has been suggested for some α-Si containing high density of impurities [10,11].

The highly doped specimens numbered 7 and 8 are of particular interest. We are not aware of any other cases where the conductivity of α-Si has been increased to such high values except for flourinated α-Si [12] and some cases where the film was thought to have changed to a microcrystalline structure [13,14]. Electron and X-ray diffraction studies of intrinsic and doped samples have failed to show any crystallinity in our material.

In the intrinsic case conduction is in the extended states characterised by a unique activation energy while some form of hopping in the delocalised states takes place in heavily doped specimens as is observed generally [15–17].

The films are stable and do not show porosity effects as observed in high pressure argon sputtered films [3.4]. No Si–O bonds have been detected by infra-red absorption or ESCA. Neon, having a smaller atomic weight than argon, and in a relatively high pressure plasma, will result in less kinetic energy of the various species bombarding the film during formation and results in a film having a lower concentration of defects. Sputtering gas is continually trapped and expelled from the silicon film during formation. The small atomic size of the neon is most likely an additional aid to the growth of films with less microvoids and included gas than is the case for argon sputtered films.

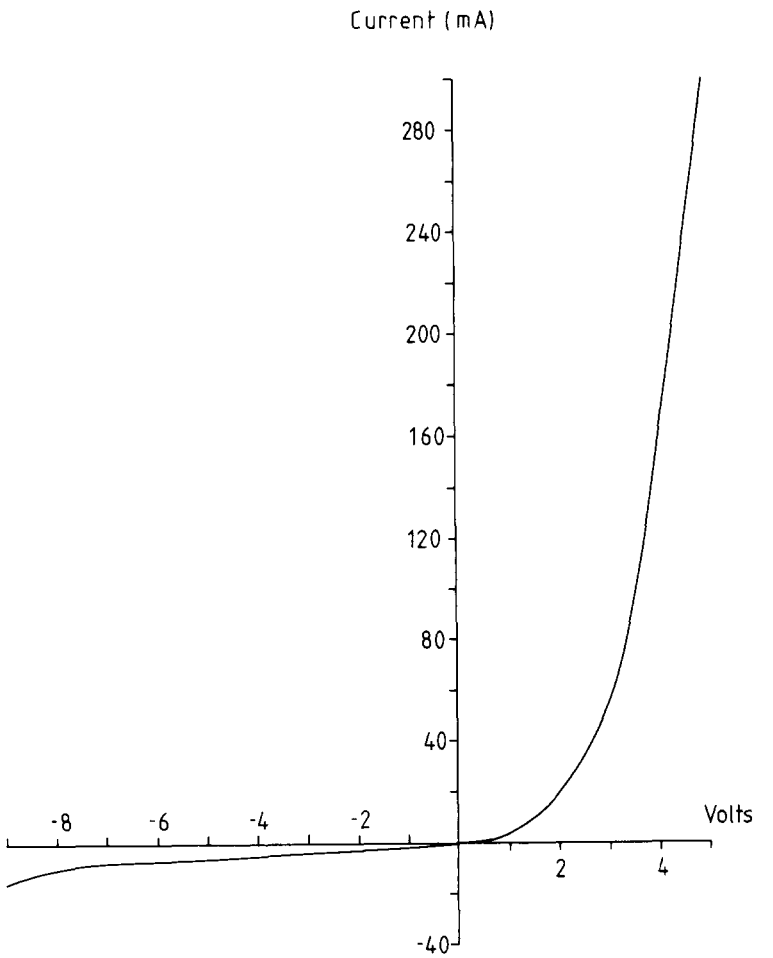

Fig. 3. Characteristic for n-type α-Si/p-type crystalline junction.

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