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DOPING EFFECTS OF GROUP III AND GROUP V ELEMENTS IN UNHYDROGENATED NEON-SPUTTERED AMORPHOUS SILICON*

S. A. ABO-NAMOUS†, Y. ZAKA AND R. W. FANE
Physics Department, University of Aston in Birmingham, Birmingham B4 7ET (Gt. Britain)

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Amorphous silicon was doped p and n type by co-sputtering with group III and group V elements. Pure neon, instead of the conventionally used $Ar-H_2$ mixture, was used as the sputtering gas. The room temperature conductivity was varied over nine orders of magnitude, with a corresponding shift in the Fermi level of about 1.2 eV in the mobility gap, without a significant change in the optical gap. Comparison of the results with those of other techniques suggests that the material has a relatively low density of defect states and a reasonable doping efficiency can be achieved. Furthermore, p–n junctions made of this material have potential semiconductor applications.

1. INTRODUCTION

In recent years amorphous silicon (a-Si) has received increasing attention because it is a promising material for low cost solar cells[1]. Amorphous silicon prepared by thermal evaporation or r.f. sputtering in argon has been known to have a high density of defect states in the mobility gap; these states hinder the doping of this material. The introduction of hydrogen, either by glow discharge decomposition of silane[2] or by sputtering in an $Ar-H_2$ atmosphere[3], satisfies the dangling bonds and relaxes the structure of the a-Si[4] resulting in a low density of states in the mobility gap. High doping efficiencies have been reported for hydrogenated a-Si (a-Si:H) doped from the gas phase by the introduction of phosphine or diborane into the discharge[5]. However, the above techniques have some disadvantages. It has been reported that hydrogen effuses at about 350 °C from films with a fairly high hydrogen concentration[6]. Also, the location of the antibonding states of the Si—H bond near the conduction band may lower the photoresponse[7]. However, recently the incorporation of halogens such as fluorine, which make stronger bonds with

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† Permanent address: Materials Application Department, Kuwait Institute for Scientific Research, Kuwait.

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silicon than does hydrogen, has resulted in a more stable a-Si:F:H alloy[8,9]. Above all, handling of the dangerous gases involved in the production of a-Si:H or a-Si:F:H makes it desirable to find a safer method of preparation. Pawlewicz[10] has reported that the properties of argon-sputtered a-Si depend strongly on the preparation conditions, such as the sputtering gas pressure, the target-to-substrate distance and the substrate temperature. A relatively low density of gap states has been reported for a-Si prepared by high pressure argon sputtering without the intentional incorporation of hydrogen or a halogen[11].

The doping efficiency of unhydrogenated argon-sputtered a-Si has been reported to depend on the preparation conditions[12]. Recently, p-type and n-type doping with aluminium and tantalum respectively have been reported for a-Si prepared by r.f. sputtering in neon[13,14], where the conductivity was varied over nine orders of magnitude, accompanied by a shift in the Fermi level of about 1.2 eV within the mobility gap. This is an indication that material with a low density of states in the gap has been produced, in support of other results on undoped a-Si[15].

In this paper doping effects of group III and group V elements in a-Si prepared by neon sputtering from a composite target or a predoped target are presented and compared with the results of doping by other techniques.

2. EXPERIMENTAL DETAILS

The details of the preparation method can be found elsewhere[13]. In brief, a-Si films were deposited in a conventional r.f. diode sputtering system using neon gas (99.999%). The target was a single-crystal wafer of electronic-grade silicon. The substrate temperature T_s was about 300 °C. The gas pressure P, the target-to-substrate distance d and the r.f. self-bias voltage V_{sb} on the target were adjusted to give a Pd/V_{sb} value of about 0.76 mTorr cm V^{-1}. It has been reported[16] that various combinations of P, d and V_{sb}, giving the same value of Pd/V_{sb}, result in films with similar properties provided that P, d and V_{sb} are kept within certain ranges[16]. A magnetic field of about 0.01 T induced by a Helmholtz pair of coils was used to collimate the discharge.

For doping, a composite target was used, where the dopant material (aluminium, boron, gallium or tantalum) was fixed on the centre of the silicon target. In the case of boron doping, pellets were made of boron powder. A boron-predoped target was also used to deposit boron-doped a-Si. Film thickness was measured using multiple-beam interferometry with an estimated error of $\pm 10\%$. Typically, the thickness of the films reported here was about 0.5 μm.

The d.c. dark conductivity was measured under vacuum using gap cell configurations with thermally evaporated aluminium electrodes separated by 1 mm. The applied electric field was 10^2 V cm^{-1}. Aluminium was found to make good ohmic contacts with a-Si films for fields up to about 10^4 V cm^{-1}.

The atomic percentage of the dopant in the silicon films was calculated from X-ray photoemission measurements (aluminium, gallium and tantalum), Rutherford backscattering spectroscopy (tantalum) and the etching profile of the target using the available sputtering yields (aluminium)[17]. In the case of boron, the superposition of the photoemission lines of silicon and boron made it very difficult

to calculate the atomic ratio of boron to silicon. However, it could be estimated that the atomic ratio of boron to silicon did not exceed the area ratio of boron to silicon. Therefore the area ratio of boron to silicon was considered to be the upper limit of the atomic ratio. The above measurements showed that the atomic ratio of aluminium to silicon is 1.15 times the target area ratio of aluminium to silicon and that the atomic ratio of tantalum to silicon is 1.8 times the area ratio of tantalum to silicon.

The type of doping was readily checked by the polarity of the thermoelectric power. P-type doping was found for aluminium-, gallium- and boron-doped films while n-type doping was found for tantalum-doped films.

3. RESULTS

The d.c. dark conductivity σ for doped a-Si films was measured as a function of temperature T in the range from -120 to 150 °C. It has been reported[13] that the plots of σ *versus* $1/T$ for lightly (less than or equal to 2.5 at.%) aluminium doped films show a singularly activated conductivity even at temperatures far below room temperature, indicating that conduction in the extended states is the dominant conduction mechanism. However, for high concentrations (2.5 at.% or more) of aluminium in a-Si, the plots of σ *versus* $1/T$ curve up at temperatures below room temperature, indicating that the hopping conduction is markedly contributing to the conduction.

The composition dependence of the room temperature conductivity σ_{RT} and of the thermal activation energy ΔE_a is shown in Fig. 1. It is seen from this figure that σ_{RT} initially decreases with increased aluminium concentration, which corresponds

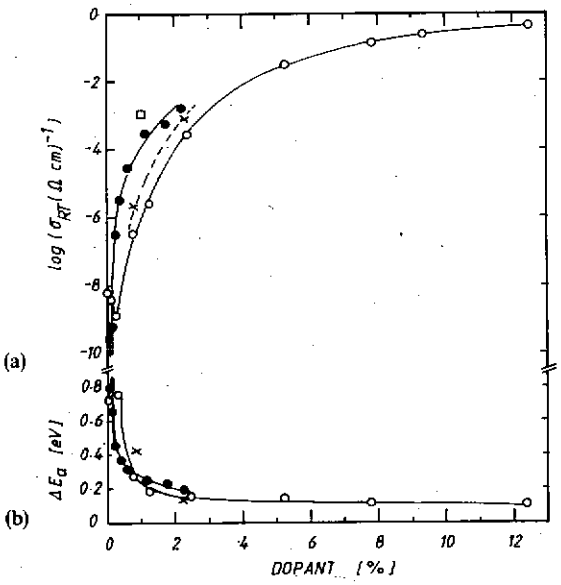

Fig. 1. Plots of (a) $\log \sigma_{RT}$ and (b) ΔE_a as functions of the dopant content in a-Si prepared by co-sputtering with aluminium (○), boron (●) or gallium (×) or by sputtering a boron-predoped target (□).

to a slight increase in ΔE_a as compensation takes place and the Fermi level moves towards the bottom of the density of states near the centre of the mobility gap, according to the Dundee group model[18]. Thereafter, σ_{RT} increases monotonically up to about 0.4 Ω^{-1} cm^{-1} with an increase in the aluminium concentration up to 12.4 at.%.

Figure 1 also shows the plots of σ_{RT} and ΔE_a as functions of the boron content in boron-doped a-Si films prepared by co-sputtering. As in the case of aluminium doping, Fig. 1 shows that initially, with the addition of a very small amount of boron to silicon (about 0.02%), σ_{RT} is reduced by at least one order of magnitude while the thermal activation energy increases to about 0.8 eV. On increasing the boron content up to 2.2% (area ratio), the room temperature conductivity increased rapidly by over seven orders of magnitude accompanied by a shift in the Fermi level position to less than 0.2 eV from the valence band. The total shift in the Fermi level within the mobility gap was about 0.7 eV.

Furthermore, sputtering from a boron-predoped silicon target, with an estimated 1 at.% B (±10%), under the same conditions as for sputtering from a composite target, gave a large change in the conductivity (up to about 10^{-3} Ω^{-1} cm^{-1}) and the thermal activation energy (down to about 0.2 eV from the valence band edge).

Since gallium has a low melting point, it was very difficult to control the required area ratio of gallium to silicon during sputtering. Accordingly, it was difficult to achieve a predetermined atomic ratio of gallium to silicon in the film and reproducibility was almost impossible. Therefore, only two specimens of gallium-doped silicon are presented here, to show the possibility of p-type doping with gallium using the co-sputtering technique. It can be seen from Fig. 1 that the room temperature conductivity of gallium-doped films increases by six to seven orders of magnitude on increasing the gallium content up to 2.2at.%. This is accompanied by a change in ΔE_a of about 0.7 eV.

The "dip" in σ_{RT} and the peak in ΔE_a in Fig. 1 are indicative of p-type doping in a-Si, since undoped films showed n-type conductivity[15].

The electrical conductivity for tantalum-doped films prepared by co-sputtering in neon was measured as a function of temperature. The tantalum concentration was varied up to 3 at.%. The variations in σ_{RT} and ΔE_a with tantalum content are shown in Fig. 2. Also shown in Fig. 2 are the variations in σ_{RT} and ΔE_a with boron content in a-Si; these values are recalled from Fig. 1 to compare the two different doping types. It can be seen from Fig. 2 that a change in the room temperature conductivity of the films over eight orders of magnitude is achieved by doping with 3 at.% Ta. Also, it can be concluded from the figure that the Fermi level moved about 1.2 eV within the mobility gap.

4. DISCUSSION AND CONCLUSIONS

The results demonstrated a variation in the room temperature conductivity over many orders of magnitude accompanied by an overall shift of 1.2 eV in the Fermi level position within the mobility gap. These variations are comparable with the best results reported for doping a-Si:H from the gas phase[5]. It should be

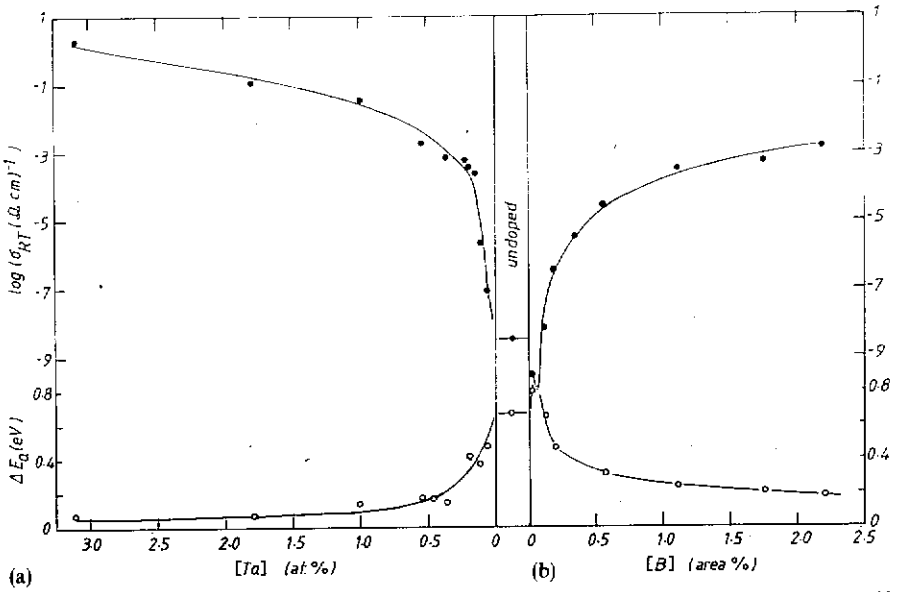

Fig. 2. Plots of log σ_{RT} (●) and ΔE_a (○) as functions of the dopant content in (a) tantalum-doped a-Si and (b) boron-doped a-Si. ([B] represents the target area ratio.)

emphasized that the optical absorption measurements showed only a slight change in the optical gap with the addition of an impurity to the a-Si [13,14]. This change, however, is expected since high doping levels may introduce defect states in the a-Si network[19]. In Fig. 3 a comparison is made between the doping efficiency of different

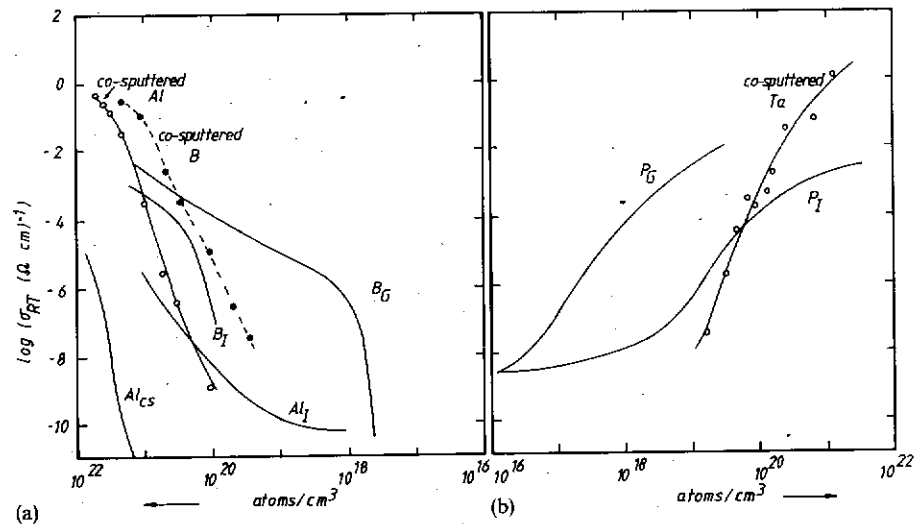

Fig. 3. Plot of log σ_{RT} as a function of the dopant concentration for (a) n-type doping and (b) p-type doping using various techniques: curves B_G, P_G, boron and phosphorus doping from the gas phase; curves B_I, P_I, boron and phosphorus doping by ion implantation[21]; curve Al_{cs}, doping with aluminium by co-sputtering in Ar–H_2 [20]; curves Al, B, Ta, co-sputtering in neon (present work).

impurities using different techniques, as indicated. The atomic concentration of dopant elements in the present films was determined using X-ray photoemission spectroscopy and/or Rutherford backscattering spectroscopy techniques as mentioned earlier. From Fig. 3 we see that, in the region of low dopant concentration, σ_{RT} for films doped by co-sputtering is generally lower than that for the gas phase doping. However, the maximum σ_{RT} of our doped samples is about two orders of magnitude higher than the maximum conductivity obtained by boron doping from the gas phase. A comparison of the doping efficiency of the same impurity for different techniques shows the following.

(i) The efficiency of boron doping by co-sputtering in neon is slightly higher than that of boron doping by ion implantation, although the former is lower than for the gas phase doping with boron at low doping levels.

(ii) σ_{RT} in the case of aluminium doping by co-sputtering in neon is a few orders of magnitude higher than that for aluminium doping by co-sputtering in an $Ar-H_2$ mixture[20].

The doping efficiency was calculated following a method explained elsewhere[13]. It has been estimated that about 1 in 800 aluminium atoms acts as an acceptor centre, which is slightly less than that for aluminium doping by ion implantation[21]. The doping efficiencies for boron doping by co-sputtering and sputtering from a boron-predoped target in neon are 1/150 and 1/75 respectively. These efficiencies are higher than those reported for boron implantation[21]. Bearing in mind that the undoped a-Si has a low room temperature conductivity (about $10^{-8}\,\Omega^{-1}\,cm^{-1}$) and a high thermal activation energy (about 0.8 eV), as well as a high photoresponse[16], the

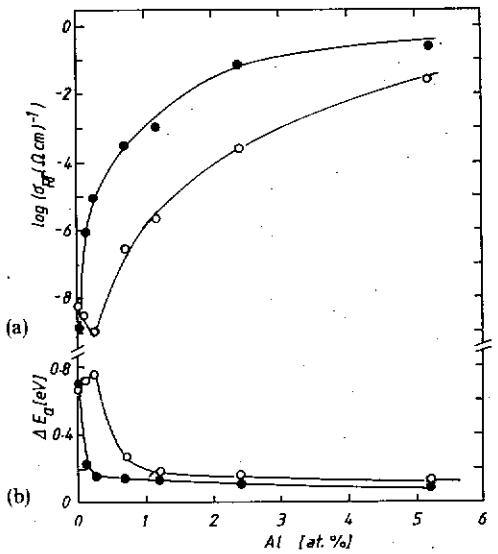

Fig. 4. Plots of (a) log σ_{RT} and (b) ΔE_a as functions of the aluminium concentration for as-deposited films (○) and films annealed at 470 °C for 90 min (●).

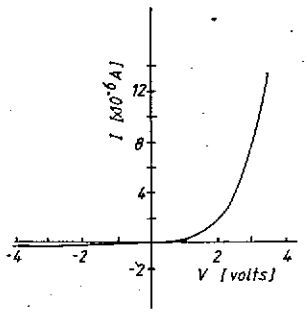

Fig. 5. Current I *vs.* voltage V characteristic curve of a typical p-a-Si/n-a-Si junction. The p-type layer is aluminium doped while the n-type layer is tantalum doped and both were prepared by co-sputtering in neon.

conclusion can be drawn that the material produced by sputtering in neon under the conditions mentioned earlier possesses a low density of states in the mobility gap. In addition, the relative doping efficiency for co-sputtering in neon compared with that for doping from the gas phase is believed to be due to the doping method rather than to the nature of the basic material. Results in support of this conclusion are shown in Fig. 4 where the aluminium doping efficiency has increased, accompanied by a reduction in ΔE_a, on annealing aluminium-doped samples at 470 °C for 90 min. Annealing undoped a-Si films resulted only in a fourfold increase in conductivity. It is highly unlikely that this is responsible for the increase of four orders of magnitude in the conductivity of the doped samples. Rather, the activation of the dopants by annealing is responsible for enhancing the doping efficiency.

It should be emphasized that p- or n-type doping, in the conventional sense, has taken place rather than an alloying effect as reported by others[20,22,23]. The control of conductivity over many orders of magnitude and the shift in the Fermi level position by about 1.2 eV, which are accompanied by a slight change in the optical gap, are in support of the above statement.

A p–n junction of aluminium-doped a-Si on tantalum-doped a-Si demonstrated reasonable rectification characteristics as can be seen in Fig. 5. This in conjunction with the photoconductive properties of a-Si[16] indicate potential semiconductor and possibly photovoltaic applications which need to be investigated in more detail.

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