Publ. V. Reunió Espanyola del Buit i les seves Aplicacions (Barcelona 1979)

Preparation of Amorphous Silicon by Sputtering in Silane

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Abstract

In the work reported here we have sputtered from silicon targets in argon-silane mixtures using undoped, n-type and p-type targets. Doped films have been produced, but the doping efficiency is extremely low. It appears that the dopant atoms are able to satisfy their natural valencies and are therefore not electrically active. Infra-red absorption spectroscopy has been used to establish the bonding system in the films. No correlation has been found between the nature of the hydrogen bonding in the film and the electrical properties.

Interstitial n-type doping has been achieved by using LiF and NaF targets. Further work is intended on these systems.

Introduction

Amorphous silicon films have been prepared by reactive R.F. sputtering from silicon and other targets in a mixture of argon and silane. The films have been characterized by measurement of their infra-red absorption spectra, in order to establish their hydrogen content, and by their electrical properties.

Experimental

An R.F. sputtering equipment was built, incorporating two target electrodes and a counter-electrode. A power-splitter enabled any ratio of R.F. power to be supplied, either to the two targets with the counter electrode earthed, or between one target and the counter electrode. The latter was provided with an electrical heater which could be used to heat the substrates up to 400°C when the counter electrode was earthed but it was not possible to heat the substrate when R.F. power was supplied to the counter electrode. A gas-flow control system enabled the argon flow-rate to be set, usually at 40 ccm. The percentage of silane was set by adjusting to the appropriate flow-rate of SiH_4 and the control system ensured that the argon/SiH_4 ratio was kept constant. The vacuum system had a background pressure of $\sim 10^{-6}$ torr and sputtering was carried out at pressures in the range 3-20 microns by adjustment of flow rate and pumping speed. The substrates used were 7059 glass, suitably cleaned, for electrical measurements and single-crystal K Br slices for infra-red measurements. Thicknesses were measured by 'Talysurf' and by multiple beam interferometry.

A magnetron target was also available. This contains the lower energy electrons near the target, reducing the electron bombardment of the substrate, and also gives higher rates of sputtering compared with the conventional system.

The silicon targets used were 3" diameter, single-crystal (111) slices doped both n- and p-type to various concentrations, supplied by Wacker Chemitronics A.G. The deposition rate from each target was determined by sputtering in pure argon. When silane is admitted, silicon is deposited from the gas at a rate determined by gas pressure and flow rate but this rate is relatively independent of sputtering power. At a pressure of 3 μm silicon is deposited from the gas at ∿.02 μm per hour per percent silane and, of course, deposits both on the substrate and on the target. When this deposition rate exceeds the sputtering rate the film obtained is pure silicon, independent of the nature of the target. With typical sputtering rates in the range 0.2-0.3μm/hr and an input power of 250 W to a 3" target, the maximum permissible silane proportion is in the range 10-15% of the total gas admitted in order for the target to contribute to the deposited film.

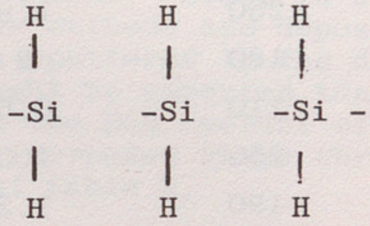
Infra-red Spectra

Absorption peaks characteristic of hydrogen bonded to silicon in the amorphous material have been studied by a number of workers(1,2,3) and table 1 gives the frequencies of the various types of bond

Table 1

Bond	Frequency (cm^{-1})	Mode
Si-H	2000	stretch
Si-H	∿640	wag
$Si = H_2$	2100	stretch
$Si = H_2$	875	bend
$Si = H_2$	∿640	wag
$(Si = H_2)_n$	850, 900 (doublet)	bend
$Si \equiv H_3$	2200	stretch
$Si \equiv H_3$	500	bend
$Si \equiv H_3$	∿640	wag

which have been identified. In films produced by glow discharge the predominant form for the hydrogen is Si-H with the principal absorption peak at 2000 cm^{-1}. For films sputtered in argon-hydrogen and argon-silane mixtures the principal peak is at 2100 cm^{-1}, indicating that the hydrogen is mainly incorporated in the double-bonded $Si = H_2$ form. Tsai and Fritzsche(3), following a suggestion by Knights(2) have shown that the double bonding is in fact often in the form of polysilane chain molecules



$$\begin{array}{ccc} H & H & H \\ | & | & | \\ -Si & -Si & -Si\ - \\ | & | & | \\ H & H & H \end{array}$$

and that these give rise to a doublet absorption at 850 and 900 cm^{-1}. In films prepared by sputtering in silane this doublet is invariably present for substrate temperatures up to 375°C. After annealing at a temperature above the deposition temperature in vacuum for several hours the 2100 cm^{-1} peak remains dominant but the doublet may be replaced by a single peak $\sim$875 cm^{-1}, suggesting that the polysilane has been broken up into separate $Si = H_2$ groups. The $Si \equiv H_3$ bending mode at 500 cm^{-1} is often observed but the stretch mode at 2200 cm^{-1} is generally obscured by the 2100 cm^{-1} peak. Annealing at 275°C normally eliminates the SiH_3 peaks.

The concentration of bonded hydrogen in the film is obtained from the area under the curve of $^{\alpha}/_{w}$ against w where α is the absorption coefficient and w is the reciprocal wavelength in cm^{-1}. Brodsky et al(1) give oscillator strengths for the various types of bond and the appropriate dielectric constant correction for their polarizabilities. Using these, the hydrogen concentrations for a typical set of sputtered films is given in table 2. In each case the deposition conditions were: flow rate 40 ccm argon, 10% SiH_4, pressure 3 μm, substrate temperature 250°C.

As sputtering rate decreases the hydrogen content increases, indicating that a larger proportion of the film originates from the silane; in fact at 100 W the sputtering rate is approximately equal to the deposition rate from the gas and the film composition is virtually independent of the nature of the target. Under these conditions it appears that the polysilane form is strongly favoured in the film.

In the glow discharge system of film deposition the plasma is produced with powers in the range 10-50 watts with gas pressures between 10^{-2} and 1 torr. Low substrate temperatures and higher

Table 2

Target	R.F. Power (watts)	Si - H ($\times10^{21}$)	$Si = H_2$ ($\times10^{21}$)	Total H ($\times10^{21}$)
0.009 Ω cm	250	1.92	1.92	3.84
n-type	180	2	4.09	6.09
	110	0.63	9.7	10.33
.007 Ω cm	250	1.07	2.14	3.11
p-type	190	1.3	3.39	4.69
	100	0.7	10.1	10.8

pressures favour the polysilane groupings. As an approach to these conditions a series of films was prepared in the sputtering system using 50 W R.F. power (below the sputtering threshold for silicon) and 10% SiH_4 with a gas pressure of 10 μm or above (10^{-2} torr.).

The results were as follows:-

(1) Substrate temperature $T_s = 250^oC$, pressure = 10μm, substrate earthed, target power = 50 W; $SiH = 1.42 \times 10^{22}$, $SiH_2 = 1.17 \times 10^{22}$.

(2) As above with pressure = 20 μm; $SiH = 1.06\times10^{22}$, $SiH_2 = 2.64 \times 10^{22}$.

Thus doubling the pressure does not increase the hydrogen content by much but increases the proportion of SiH_2.

(3) Specimen (2) annealed at 285°C in a vacuum of 10^{-6} torr. for 4 hrs; $SiH = 3.28 \times 10^{21}$, $SiH_2 = 8 \times 10^{21}$, i.e. both the SiH and SiH_2 content were lowered by a factor of 3.3, their ratio remaining unchanged.

(4) $T_s = 25^oC$, target earthed, substrate power 50 W, pressure 10 μm, $SiH = 1.3 \times 10^{22}$, $SiH_2 = 0.85\times10^{22}$. Thus deposition on the cathode enhances the SiH peak, compared with the SiH_2.

(5) Specimen (4) was annealed as above; $SiH = 4\times10^{21}$, $SiH_2 = 1.5 \times 10^{21}$, i.e. the total hydrogen content is decreased and the SiH/SiH_2 ratio is increased.

(6) $T_s = 25^oC$, target power 30 W, substrate power 30 W, pressure 10 μm; $SiH = 2.83 \times 10^{22}$, $SiH_2 = 1.82 \times 10^{22}$. The total hydrogen content is increased compared with the cathode case (specimen 4) but the SiH/SiH_2 ratio is

slightly smaller.

(7) Specimen (6) annealed as above; SiH = $1.73\text{x}10^{22}$, SiH_2 = $9.3 \text{ x } 10^{21}$, i.e. the hydrogen content is decreased and the SiH/SiH_2 ratio increases.

Summarizing the above it is evident that deposition on the cathode favours Si-H bonding over the doubly bonded form. Since in normal sputtering the target is the cathode and deposition onto it from the silane is re-sputtered in the direction of the substrate, it might be expected that there will be some increase in the SiH content of the films as the sputtering rate increases above threshold, as shown in the results of table 2.

Electrical Properties

The standard measurement adopted was of conductivity as a function of temperature in order to obtain the activation energy for conduction. Contacts used were Cr or AuSb for n-type films and Aℓ for p-type films. Spear and Le Comber(4) obtained doped films by glow discharge deposition from mixtures of phosphine and silane for n-type and borane and silane for p-type. From their results the density of electrically active donors or acceptors can be obtained approximately from the measured activation energy. However, they found that "intrinsic", undoped silicon films gave defect-controlled conductivity with activation energies in the range 0.6-0.7 eV. In the present work, pure silicon films have been found to give activation energies in the range 0.7-0.8 eV. In table 3 we give the electrical results for the films of table 2.

Table 3

Target	Power (W)	Total Rate (µm/hr)	Sputter Rate (µm/hr)	E_A (eV)	Dopant/ Silicon Ratio
n^+	250	0.54	0.4	0.61	$7\text{x}10^{-6}$
	180	0.37	0.23	0.8	$5.8\text{x}10^{-6}$
	110	0.25	0.11	0.75	$4.1\text{x}10^{-6}$
p^+	250	0.62	0.48	0.55	$2.8\text{x}10^{-5}$
	190	0.56	0.42	0.7	$2.3\text{x}10^{-5}$
	100	0.36	0.22	0.7	$2.17\text{x}10^{-5}$

Only the 250 W specimens exhibit extrinsic conductivity. Using Spear and Le Comber's results E_A = 0.61 eV for an n-type specimen corresponds to a ratio of $3 \text{ x } 10^{-7}$ active donors to silicon atoms. On this basis only one in 23 of the sputtered phosphorous atoms from the n^+ target are electrically active in the film. For the p^+ film Spear and Le Comber's results suggest an active boron to silicon ratio of 2.5×10^{-5} which would indicate that almost every boron atom in the sputtered film is electrically active. To investigate this point further, films were prepared using a pure boron target with varying silane concentrations. At 5% silane, $T_S = 250^oC$, pressure = 0.4 μm, a film containing 23% boron was obtained with an activation energy of 0.53 eV. This would correspond to a doping fraction 2×10^{-5} from Spear and Le Comber's results, suggesting that only about one in 10,000 of the boron atoms are electrically active.

The general conclusion from this work is that when the dopant is incorporated by sputtering from a doped target it is mostly able to satisfy its valency in the deposited film and, as a result, is in the main not an electrically active substitutional dopant.

Interstitial Doping

In view ofthe inefficiency of substitutional doping it was decided to examine the possibility of interstitial doping. Ovshinsky and Madan(5) have reported that fluorine behaves similarly to hydrogen in α-silicon films in taking up dangling bonds and further that doping efficiency is increased by the presence of fluorine.

Films were prepared by using an LiF target and varying silane percentages with $T_S = 250^oC$ and 350 W R.F. power. The rate for LiF in 4μ of pure argon was 0.12 μm/hr from a 2" diameter target but the presence of silane appeared to alter this rate and, in fact, both 2.5% and 5% SiH_4 gave the same total deposition rate of 0.25 μm/hr. It is therefore impossible to determine the lithium content of the film without chemical analysis. However, activation energies in the region of 0.5 eV with conductivities of $\sim 5 \times 10^{-8}$ Ω cm at room temperature were obtained with 2.5 and 5% SiH_4.

A set of films was also produced using a NaF target. A typical result for 10% SiH_4 and similar conditions to the LiF case gave an activation energy of 0.47 eV with conductivity of 4×10^{-5} Ω cm at room temperature.

Clearly, interstitial doping can be effective and further work on both lithium and sodium doping is in hand.

Intrinsic Films

Activation energies for the low power, high pressure films described earlier were found to lie in the range 0.73 to 0.86 eV. There was no correlation between these conductivities or activation energies and the amount of hydrogen incorporated or the form of bonding of the hydrogen. Whilst intuitively it would seem that singly bonded SiH should give the best electrical behaviour no evidence has yet been found to support such a view.

Conclusions

Substitional doping of α-silicon films by sputtering deposition from doped targets in the presence of silane is inefficient over the normal range of sputtering conditions. There is no evidence that this is associated with the predominance of the $Si-H_2$ bonded form of hydrogen in the films. Since doping from the gaseous hydrides has been shown to be effective in both sputtering and glow discharge depositions, it may be assumed that the dopant atom must carry an H atom with it into the film in order to achieve an electrically active substitutional site.

From limited experiments it appears that interstitial n-type doping by lithium or sodium atoms in the presence of fluorine may be more effective. Further work is necessary on this system.

Acknowledgements

It is a pleasure to acknowledge the valuable assistance of R. Chater of the Analytical Services Laboratory of Imperial College, who carried out the infra-red spectroscopy.

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