

Preparation of Amorphous Silicon by Sputtering in Silane

(사이렌 기체속에서 스퍼터한 非晶質 硅素의 性質)

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要 約

도핑안된 n- 또는 p-형 硅素標的으로부터 알곤과 사이렌(Si, H₄) 혼합기체 속에서 스퍼터한 결과를 보고한다. 도핑된 박막이 생성되었다. 그러나 도핑효율을 극히 낮았다. 이것은 도판트 원자가 그들 본래의 가(價)에 만족하고 전기적으로 활성이 아니라고 할 수 있겠다.

赤外線吸收分光法으로 박막내에 수소가 결합되어 있음을 알 수 있었다. 박막내에서 수소의 결합과 전기적성질사이에 어떤 관계가 있다고는 밝혀지지 않았다.

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 hydrogen bonding in the films. No correlation has been found between the nature of the hydrogen bonding in the film and the electrical properties.

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 characterised 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

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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 KBr slices for infrared 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, singlecrystal (III) 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 all 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 0.2-0.3 $\mu\text{m/hr}$ 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.

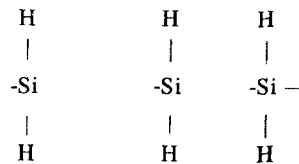
Infra-red Spectra

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 200 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⁾ deduced that the double bonding is in fact often in the form of polysilane chain molecules



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 $\sim 875 \text{ cm}^{-1}$, suggesting that the polysilane has been broken up into sepa-

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rate Si = H₂ groups. The Si = H₃ 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 270°C normally eliminates the SiH₃ peaks.

The concentration of bonded hydrogen in the film is obtained from the area under the curve of α/ω against ω where α is the absorption coefficient and ω is the reciprocal wavelength in cm⁻¹. Brodsky et al.^[11] give oscillator strengths for the various types of bond and the appropriate dielectric constant correction for their polarisabilities. 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, 7½% SiH₄, pressure 3 μm, substrate temperature 250°C. A typical absorption spectrum for 100 W is shown in figs. 1(a) and 1(b).

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 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% SiH₄ with a gas pressure of 10 μm or above (10⁻² torr).

In figs. 2(a) and (b) are shown the spectra, plotted as α/ω against ω , for a film deposited

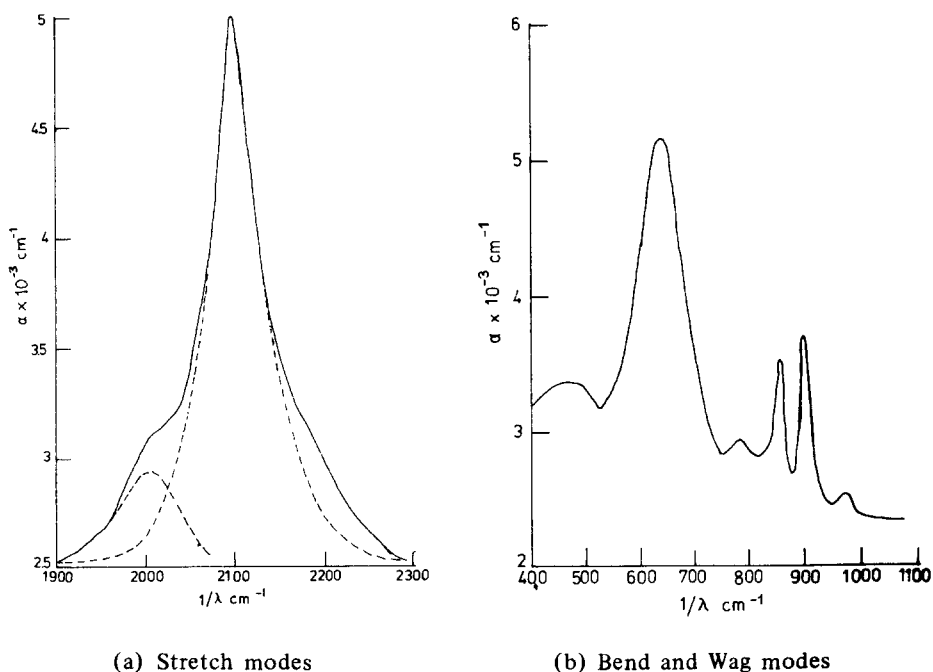


Fig. 1. I.R. absorption spectra for sputtered films.

As sputtering rate decreases the hydrogen content increases, indicating that a larger proportion of the film originates from the

on the earthed counter-electrode (anode) at 10 μm and 20 μm total gas pressure with $T_s = 250^\circ\text{C}$. Also shown are the spectra re-

Table 2.

Target	R.F. Power (watts)	Si - H ($\times 10^{21}$) cm^{-3}	Si = H ₂ ($\times 10^{21}$) cm^{-3}	Total H ($\times 10^{21}$) cm^{-3}
0.009 Ω cm n-type	250	1.92	1.92	3.84
	180	2	4.09	6.09
	110	0.63	9.7	10.33
.007 Ω cm p-type	250	1.07	2.14	3.11
	190	1.3	3.39	4.69
	100	0.7	10.1	10.8

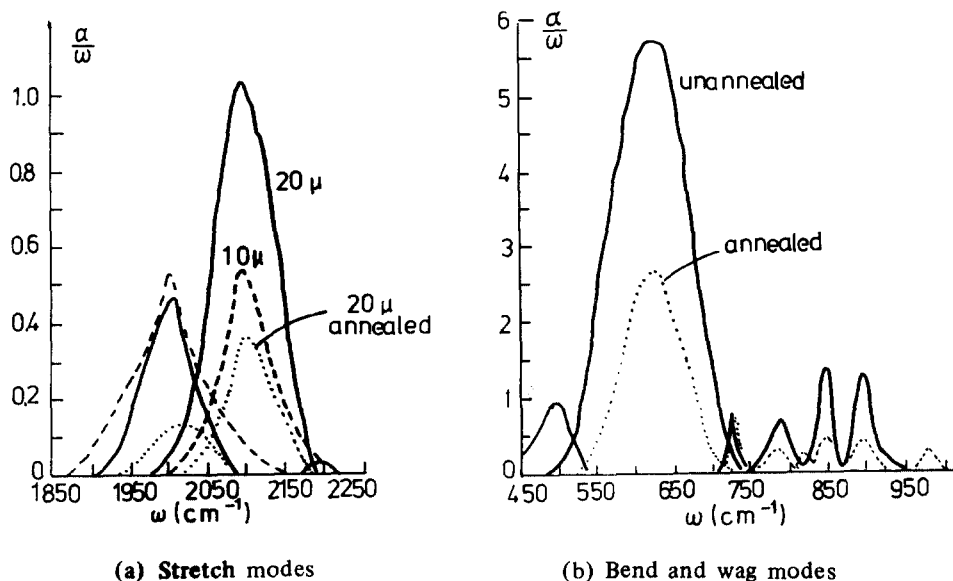


Fig. 2. I.R. absorption spectra for low-power, high-pressure films.

sulting from annealing the 20 μm film at 285°C for 1 hr in a vacuum of 10^{-6} torr. It will be seen that the SiH_2 doublet at 850-900 cm^{-1} is reduced by annealing but remains a doublet. The SiH_3 peaks at 2200 and 500 cm^{-1} disappear after annealing. These results were compared with those obtained using identical conditions and a pressure of 10 μm but with a magnetron target, which much reduces electron bombardment of the growing film. No significant differences were found in the resulting spectra, the amount of hydrogen incorporated or its distribution between bonding states.

In figs. 3(a) and (b) the spectra for a film deposited on the cathode electrode at $T_s = 25^\circ\text{C}$ at a pressure of 10 μm are shown for the as-deposited film (solid line) and after annealing at 285°C for 1 hr (dotted line). The large peak at 975 cm^{-1} in the as-deposited film is not recognised but, since it completely disappears on annealing, is assumed to be due to a gaseous silicon-hydrogen molecule. As found by Tsai and Fritzsche^[3], the principal form of bonding appears to be SiH . The SiH_2 doublet of the anode films is replaced by a singlet at 875 cm^{-1} , indicating that the polysilane form is absent. SiH_3 groups appear to be completely

absent.

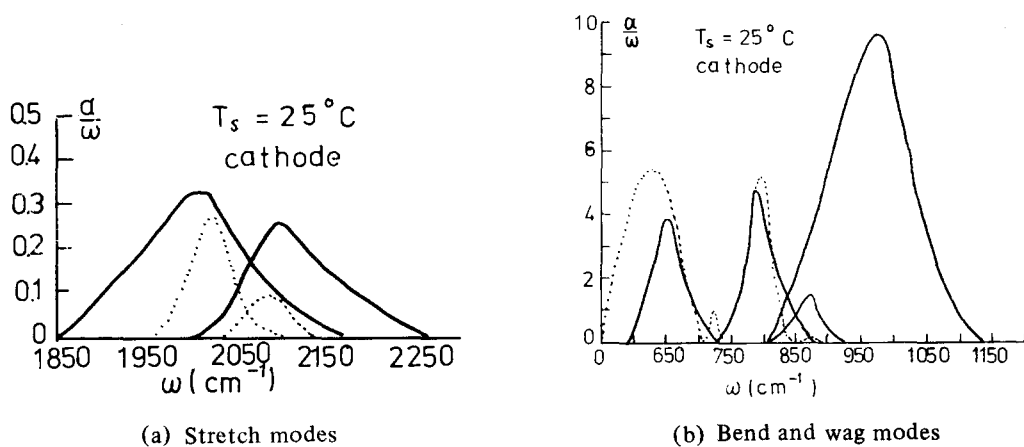


Fig. 3. I.R. absorption spectra for films.

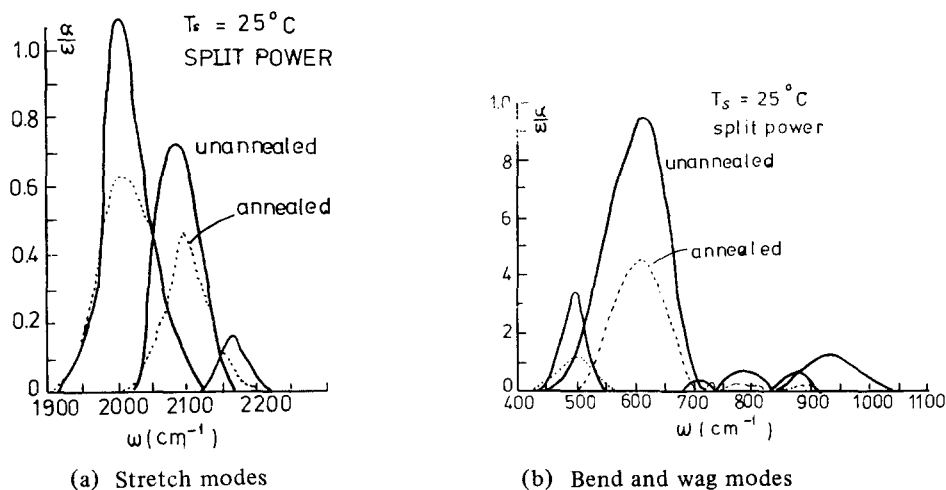


Fig. 4. I.R. absorption spectra for films deposited with split power (see text).

In figs. 4(a) and (b) are shown the spectra for the case where the power was split equally between target and counter-electrode (30 W in each), with the substrate on the counter-electrode at a temperature of $T_s = 25^\circ\text{C}$, with $10\ \mu\text{m}$ gas pressure. It will be seen that the SiH peak at $2000\ \text{cm}^{-1}$ still predominates but that the SiH₂ peak is stronger than in the cathode case. The unidentified peak at 975

cm^{-1} is again present, but much weaker, and disappears on annealing. The SiH₂ bend mode is a singlet at $875\ \text{cm}^{-1}$. An SiH₃ peak is visible for both the stretch mode ($2200\ \text{cm}^{-1}$) and the bend mode ($500\ \text{cm}^{-1}$) in the as-deposited film and is still present, although reduced, after annealing.

Oscillator Strengths

These results present an opportunity for estimating the oscillator strengths for the bending and wagging modes for the SiH₂ and SiH₃ groups.

Brodsky et al^[1] (hereafter referred to as BCC) point out that the peak at 2100 cm⁻¹ arises from both the SiH₂ stretch mode and the symmetric SiH₃ stretch mode whilst the peak at 2200 cm⁻¹ corresponds to the asymmetric SiH₃ stretch mode. The films of fig. 2 show both a well-resolved peak at 2200 cm⁻¹ and one at 500 cm⁻¹, which we believe to be due to the SiH₃ bend mode. BCC give, for the number of bonds in a stretch mode,

$$N = \frac{(1+2\epsilon_m)^2}{9\epsilon_m^2} \epsilon_m^{1/2} \frac{N_0}{\Gamma/\zeta} \int \frac{\alpha(w)}{w} dw \dots\dots\dots (1)$$

where ϵ_m is the relative permittivity, N_0 is Avogadro's number, Γ/ζ is the oscillator strength per bond and the integral is the area under the peak. They quote $\Gamma/\zeta = 3.5$ cm²/m.mol. for the stretch mode in all groups. Applying this to the 2200 cm⁻¹ peak of Fig. 2 we find the number of SiH₃ bonds to be 7.47×10^{21} cm⁻³. Using this with the area of the 500 cm⁻¹ peak gives an oscillator strength per group for SiH₃ of 26.8 cm²/m.mole; this compares well with the average figure of 28 cm²/m.mol. quoted by B.C.C. for the bending mode. We choose an average figure of 27 cm²/m.mol.

Using the SiH₃ concentration deduced we may determine the concentration of SiH₂ bonds from the area under the 2100 cm⁻¹ peak with the SiH₃ contribution subtracted. Using this, with the area under the 875-900 cm⁻¹ doublet we deduce a figure for the bending mode oscillator strength per SiH₂ group of 7.08 cm²/m.mol. which is close to the figure of 7 cm²/m.mol quoted by B.C.C.

Using these oscillator strengths, namely SiH = 3.5, SiH₂ = 7 and SiH₃ = 27 cm²/m.mol. We can obtain the concentration of these groups in our films from the 2000 cm⁻¹, 850-900 cm⁻¹ and 500 cm⁻¹ peaks respectively.

The peak at 640 cm⁻¹ is ascribed to the wagging mode of all three groupings. We assume that the total area, A_{640} , under the peak can be represented as the sum of the areas due to the three modes separately. Thus

$$A_{640} = \Gamma_1^w \frac{N_1}{B} + \Gamma_2^w \frac{N_2}{B} + \Gamma_3^w \frac{N_3}{B} \dots\dots (2)$$

where B is a constant given by $\frac{9\epsilon_m^{3/2} N_0}{(1 + 2\epsilon_m)}$

and $\Gamma_1^w, \Gamma_2^w, \Gamma_3^w$ are the oscillator strengths for SiH, SiH₂ and SiH₃ respectively. Using a linear regression analysis with eqn. (2) on all the specimens described here we find $\Gamma_1 = 47, \Gamma_2 = 56$ and $\Gamma_3 = 198$ cm²/m-mol for the singly, doubly and trebly bonded groups respectively. However, B.C.C. point out that due to uncertainty in the scaling of the permittivity to account for local field corrections, the estimates for hydrogen bond concentration are unlikely to be accurate to better than within a factor of 2. Thus the absolute figures derived above are subject to the same accuracy. Even allowing for this it would appear from the results that the contribution from each bond in the SiH₂ and SiH₃ groups is not equal to the contribution of an SiH bond alone.

Summarising 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 increase 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

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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.

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.

Intrinsic Films

Activation energies for the low power,

Table 3.

Target	Power	Total Rate	Sputter Rate	E_A	Impurity/ Silicon Ratio
	(W)	($\mu\text{m/hr}$)	($\mu\text{m/hr}$)	(eV)	
n ⁺	250	0.54	0.4	0.61	7×10^{-6}
	180	0.37	0.23	0.8	5.8×10^{-6}
	110	0.25	0.11	0.75	4.1×10^{-6}
p ⁺	250	0.62	0.48	0.55	2.8×10^{-5}
	190	0.56	0.42	0.7	2.3×10^{-5}
	100	0.36	0.22	0.7	2.17×10^{-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 3×10^{-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 show an initial compensation occurring as the p-type dopant is introduced so that converting from an activation energy to a dopant concentration is uncertain for lower dopant concentrations. To investigate this point further, films were prepared using a pure boron target with varying silane concentrations. At 5% silane, $T_s = 250^\circ\text{C}$, pressure = $0.4 \mu\text{m}$, a film containing 23% boron was

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

Substitutional doping of α -silicon films by sputter-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-H₂ 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 the case that the dopant atom must carry an H atom with it into the film in order to achieve an electrically active substitutional site.

References

1. M.H. Brodsky, M. Cardona and J.J. Cuomo, Phys. Rev. B. 16, 3556 (1977).
2. J.C. Knights, Phil. Mag. 34, 663 (1976)
3. C.C. Tsai and H. Fritzsche, Solar Energy Matls. 1, 29 (1979).
4. W.E. Spear and P.G. Le Comber, Phil. Mag. 33, 935 (1976).

