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The optical joint density of states of amorphous silicon nitride

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Received 27 April 1989

Abstract. Reflectivity measurements have been made in the range 0.5–12 eV on amorphous silicon nitride films containing various concentrations of nitrogen. Films prepared by radio-frequency sputter deposition of silicon in an argon/nitrogen plasma, both with and without hydrogen, were studied along with films prepared by the glow-discharge technique. From the reflectivity data, ϵ_1 - and ϵ_2 -spectra were determined using Kramers–Krönig analysis and, from the latter, the optical joint densities of states (OJDOS) were derived. The behaviour of the OJDOS and its variation with nitrogen content in the films is discussed in terms of the valence band density of states and its change on alloying.

1. Introduction

Amorphous SiN_x is used extensively in the microelectronics industry both as a passivating layer and as an active component in metal–nitride–oxide–semiconductor FETS. A detailed study of the electronic structure of hydrogenated films of a- SiN_x ($0 \leq x \leq 1.6$) has been reported by Karcher *et al* (1984) using measurements of photoemission from sputtered and glow-discharge samples in an attempt to clarify the nature of the defect states and to determine the evolution of the valence band density of states as a function of x . Optical absorption and luminescence measurements have been made on glow-discharge samples by Austin *et al* (1986) and have been summarised by Searle (1987). Optical properties and spin-resonance signals in sputtered and glow-discharge samples have been reported by Davis *et al* (1987) and by Piggins *et al* (1987). Stewart and Jones (1988) have used photothermal deflection spectroscopy to study defect absorption in glow-discharge SiN_x .

In this paper we present reflectivity measurements in the photon energy range 0.5–12 eV from which we deduce the optical joint density of states (OJDOS) as a function of nitrogen content x ($0 < x < 1.4$) in amorphous films of a- SiN_x . Three sets of films have been studied: (i) films prepared by glow-discharge decomposition of SiH_4/NH_3 mixtures (kindly provided by Professors W E Spear and P G Le Comber, University of Dundee); (ii) films prepared by RF sputtering of crystalline Si in argon/nitrogen/hydrogen mixtures; and (iii) films prepared by RF sputtering of crystalline argon/nitrogen mixtures.

The principal objectives of the work are to investigate how the various silicon and nitrogen levels might contribute to the valence band density of states as x is increased and to decide if the presence of hydrogen in the films plays any role in this evolution.

2. Experimental procedure

The sputtered films were prepared from a 99.999% pure polycrystalline silicon target in an argon–nitrogen (–hydrogen) plasma using an RF power of 200 W and a chamber pressure of 10 mTorr. The relative nitrogen (and hydrogen) flow rates were adjusted to control the composition of the films, which was determined by Rutherford back-scattering (RBS) and electron microprobe analysis (EMPA)†. Details of the method for preparing the glow-discharge films can be found in Dunnett *et al* (1986).

Near-normal-incidence reflectivity measurements were made in the range 0.5–5 eV using a Perkin–Elmer 330 spectrometer and from 5–12 eV using a vacuum–ultraviolet spectrometer at the Cavendish Laboratory (see Shen (1987) for details of the VUV spectrometer). Plasma energies were determined from a separate experiment on sputtered films using x-ray photoelectron spectroscopy. Monochromatised Al K α (1486.6 eV) radiation was used for photoexcitation. The electrons emitted from the sample were collected and energy analysed using an integrating retarding-field hemispherical analyser. These experiments were performed under ultra-high vacuum working at a pressure of 10^{-10} Torr.

3. Data analysis

The optical constants were obtained from the reflectivity spectra using Kramers–Kronig analysis. This method requires a knowledge of the reflectance over a large (in principle, infinite) energy range. Two extrapolations were made to extend our data range. For energies below the first data point (0.5 eV), a constant reflectivity was assumed. This is justified since this energy lies well below the onset of the optical absorption edge in all films. The extrapolation at high energies needs to be chosen with care, since there is clearly a large contribution to the integral beyond the last data point. If it is assumed that the real part of the dielectric constant, ϵ_1 , is given by the Drude formula for energies E well above the plasma energy E_p , then $\epsilon_1 = 1 - (E_p/E)^2$. At high energies, $\epsilon_2 \rightarrow 0$ and so the refractive index $n = \epsilon_1^{1/2} \sim 1 - \frac{1}{2}(E_p/E)^2$. The reflectivity $R = (n - 1)^2/(n + 1)^2$ is then $\frac{1}{16}(E_p/E)^4$ for $E \gg E_p$. The highest measured energy E_H (12 eV) in our reflectivity spectra is less than E_p and so we cannot use this relationship to obtain absolute values of reflectance. Nevertheless we have chosen to use the quartic relation and have extrapolated the reflectance using the relation $R = R_H(E_H/E)^4$ where R_H is the reflectivity measured at E_H .

The variation of n and k with photon energy $E = \hbar\omega$ are then obtained from the dispersion relation

† The RBS measurements were made by C Jeynes at the University of Surrey and the EMPA by M Poole at Harwell.

$$\theta(\omega) = \frac{-\omega}{\pi} \int_0^{\infty} \frac{\ln(R(\omega')/R(\omega)) d\omega'}{(\omega'^2 - \omega^2)}$$

and the equations

$$n(\omega) = (1 - R(\omega))/[1 + R(\omega) - 2(R(\omega))^{1/2} \cos \theta(\omega)]$$

$$k(\omega) = 2(R(\omega))^{1/2} \sin \theta(\omega)/[1 + R(\omega) - 2(R(\omega))^{1/2} \cos \theta(\omega)].$$

ε_1 and ε_2 are then obtained from n and k via the well known relationships $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$. From the ε_2 -spectra the OJDOS is obtained from $E\varepsilon_2$ in states eV^{-1} per SiN_x formula unit. The matrix elements were taken to be unity throughout the whole energy range.

Sum rules are very useful in the interpretation of optical data. A sum rule that relates the effective number of electrons, n_{eff} , contributing to the optical constants up to an energy E_c is

$$\int_0^{E_c} E\varepsilon_2(E) dE = E_p n_{\text{eff}}$$

where E_p is the plasma energy, $= \hbar\omega_p$. This equation has been used to calculate n_{eff} using the values of E_p determined by photoemission from core levels. The values of n_{eff} thus obtained were then considered with respect to the expected number of valence electrons, which provides a test of the validity of the extrapolations used in the KK analysis.

4. Results

Figure 1 shows the reflectivity, measured at room temperature, for the three sets of samples studied. It will be observed that variations between films prepared by the three different methods are not great and we conclude that hydrogen does not have a *significant* effect on the overall form of the spectra. For all spectra, the principal broad peak that lies near 5 eV for low values of x decreases in height and at first shifts slightly to lower energies with increasing x . For $x > 1$, this peak is replaced by a similar but broader feature peaking at energies above 7 eV.

The spectral dependences of the real (ε_1) and imaginary (ε_2) parts of the dielectric constant are shown in figures 2 and 3. For low x the ε_1 -data show a relatively sharp resonance and suggest that the plasma energy (where ε_1 approaches zero) is about 12 eV. This is lower than values from photoemission data (shown in figure 6) owing to damping associated with electron–electron scattering. With increasing x the resonance becomes much broader and the plasma energy shifts to higher values for all types of film.

The ε_2 -spectra exhibit a sharper peak than in the reflectivity data, with the maximum occurring at 4 eV for $x = 0$ in all three types of film. As x increases the peak height drops quite markedly and shifts monotonically to higher energies. This shift is more rapid for $x > 0.5$ and the peak position reaches ≈ 8 – 10 eV in the films with the highest x (close to the stoichiometric composition of Si_3N_4 , i.e. $x = 1.33$), at which point the peak is considerably broadened.

The OJDOS spectra (figure 4) show a similar variation to that of ε_2 with increasing x . Here it seems worthwhile to point out that the spectra beyond ≈ 9 eV are all very similar—almost independent of x or the method of film preparation.

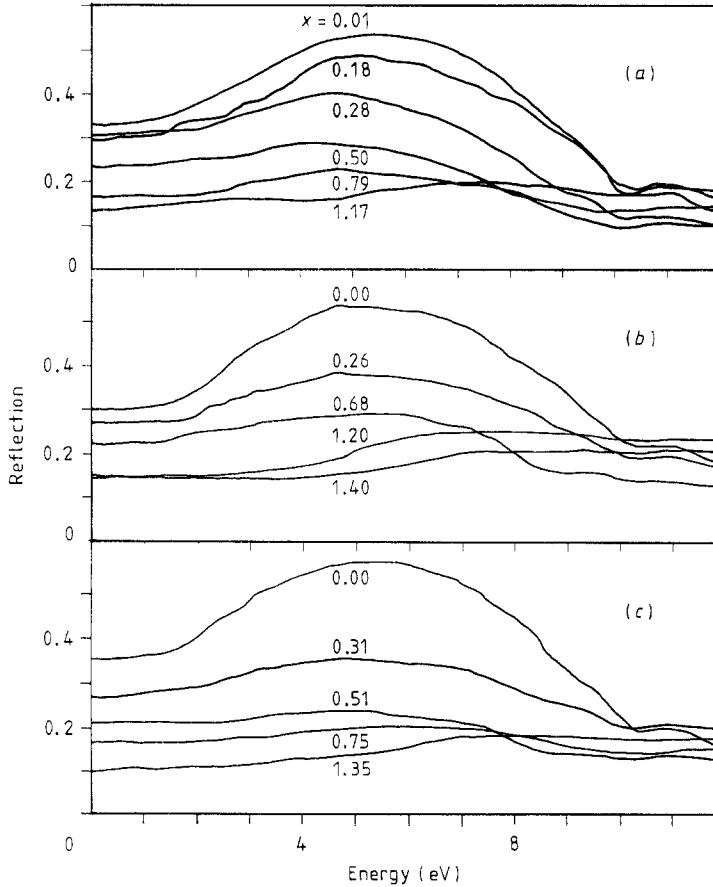


Figure 1. Room-temperature reflectivity spectra of a-SiN_x (:H) films as a function of x . (a) Glow discharge; (b) sputtered (hydrogenated); (c) sputtered (no hydrogen).

Figure 5 displays n_{eff} versus photon energy as determined from the integral given in § 3. One should note that n_{eff} does not reach the expected value of four (for $x = 0$) at the highest energy measured but this is not expected until $E = E_p$. The plasma energy E_p is shown in figure 6. This variation agrees well with that reported by Karcher *et al* (1984). As x increases, n_{eff} decreases throughout the whole measured spectral range and at $E = 12$ eV falls well below four. This is to be expected since the average number of valence electrons per atom falls as the proportion of trivalent nitrogen increases and also the plasma energy increases with x to values greater than 16 eV.

5. Discussion

The shift in the main peak in the OJDOS spectra is partly due to the increase in the band gap of the alloys as x is increased. The variation of the optical gap, determined from a Tauc plot, is known to depend on the hydrogen content. Figure 7 reproduces data reported in Davis *et al* (1987). The increase of E_T with nitrogen content is seen to be slow for low x but rises dramatically when $x > 1$. Furthermore, hydrogenated films

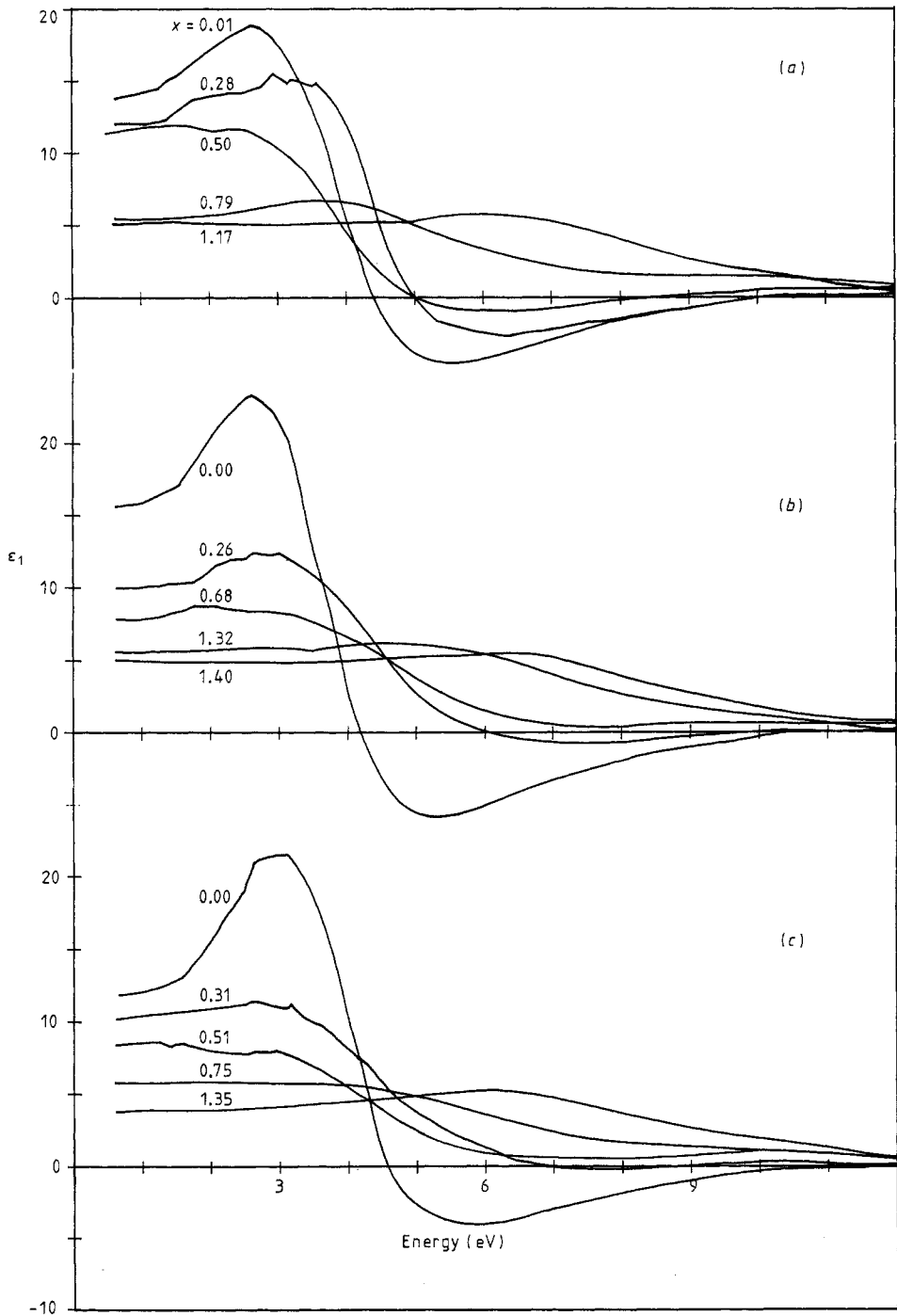


Figure 2. The real part (ϵ_1) of the dielectric constant as a function of photon energy for $a\text{-SiN}_x(\text{H})$ films as a function of x . (a) Glow discharge; (b) sputtered (hydrogenated); (c) sputtered (no hydrogen).

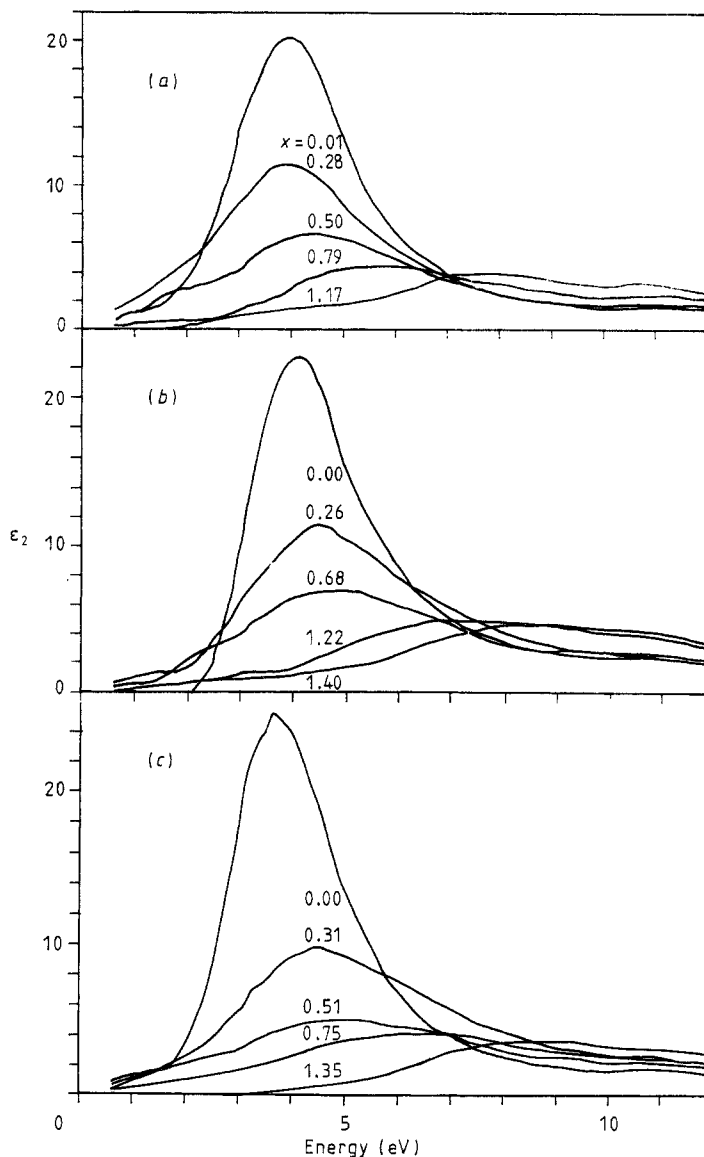


Figure 3. The imaginary part (ϵ_2) of the dielectric constant as a function of photon energy for a-SiN $_x$ (:H) films as a function of x . (a) Glow discharge; (b) sputtered (hydrogenated); (c) sputtered (no hydrogen).

(prepared either by sputtering or glow discharge) have initially a larger gap than unhydrogenated films, but beyond $x \approx 1$ the gaps of all materials converge. Similar results for glow-discharge films have been reported by Lowe *et al* (1986). Other workers (see, for example, Stotzel 1987), find a more drastic increase in E_T beyond $x = 1$ and the gap of a-Si $_3$ N $_4$ is probably between 4 and 5 eV.

The rather surprising result is that, at first sight, the DOVS of a-SiN $_x$ films does not show any evidence of replacement of a silicon-based valence band by one that contains a significant contribution from N-derived states. Interestingly a rather similar evolution

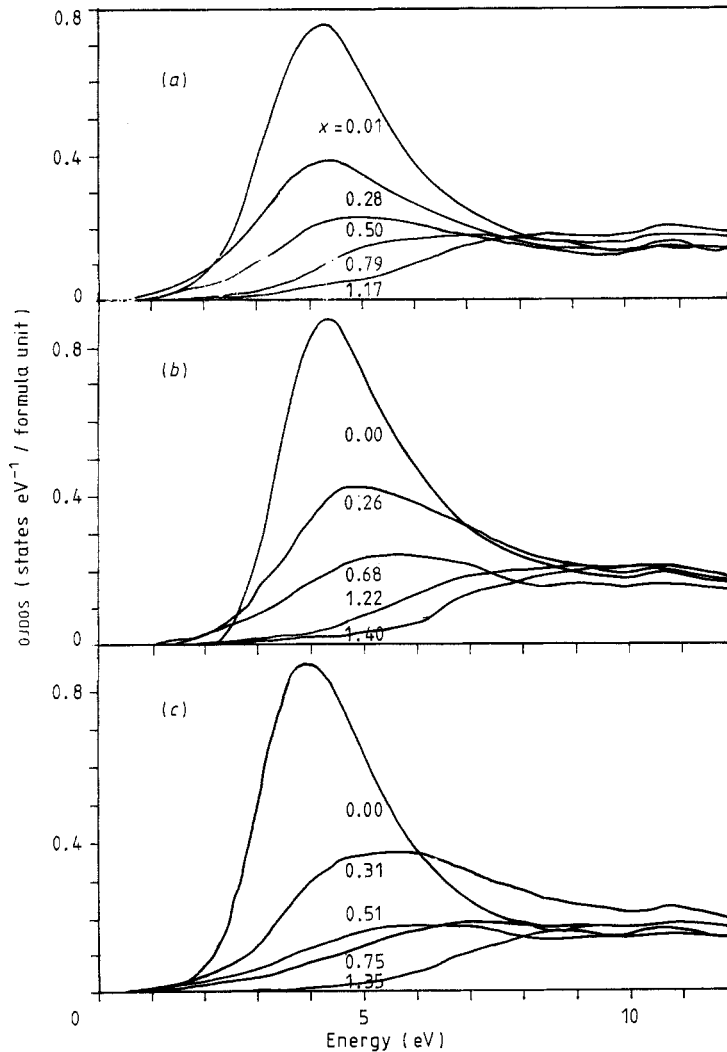


Figure 4. The optical joint density of states (OJDOS) for a-SiN_x(:H) films as a function of *x*. (a) Glow discharge; (b) sputtered (hydrogenated); (c) sputtered (no hydrogen).

of the ϵ_2 -spectra was observed by Sotiropoulos and Weiser (1987) in a-SiC_x:H alloys with increasing C content. These authors remark on the retention of the silicon-like spectra beyond values of *x* at which Si-C bands or C-C bands would be expected. Their explanation was that the hydrogen bonds preferentially to the C atoms leaving the Si network fairly intact, at least until $x \sim 0.7$. This argument cannot of course be used for our *unhydrogenated* films.

Calculations of the electronic structure of Si₃N₄ using tight-binding methods have been made by Lucovsky and Lin (1985), Robertson (1984) (see Karcher *et al* 1984), San Fabian *et al* (1989), and Martin-Moreno *et al* (1987). The results of Lucovsky and Lin (1985) are reproduced in figure 8, which shows the average density of states (DOS) for a Si₃N₄ Bethe lattice and the component local DOS for the nitrogen 2p and 2s states and the silicon 3p and 3s states. It is seen that, as far as the valence band is concerned, the

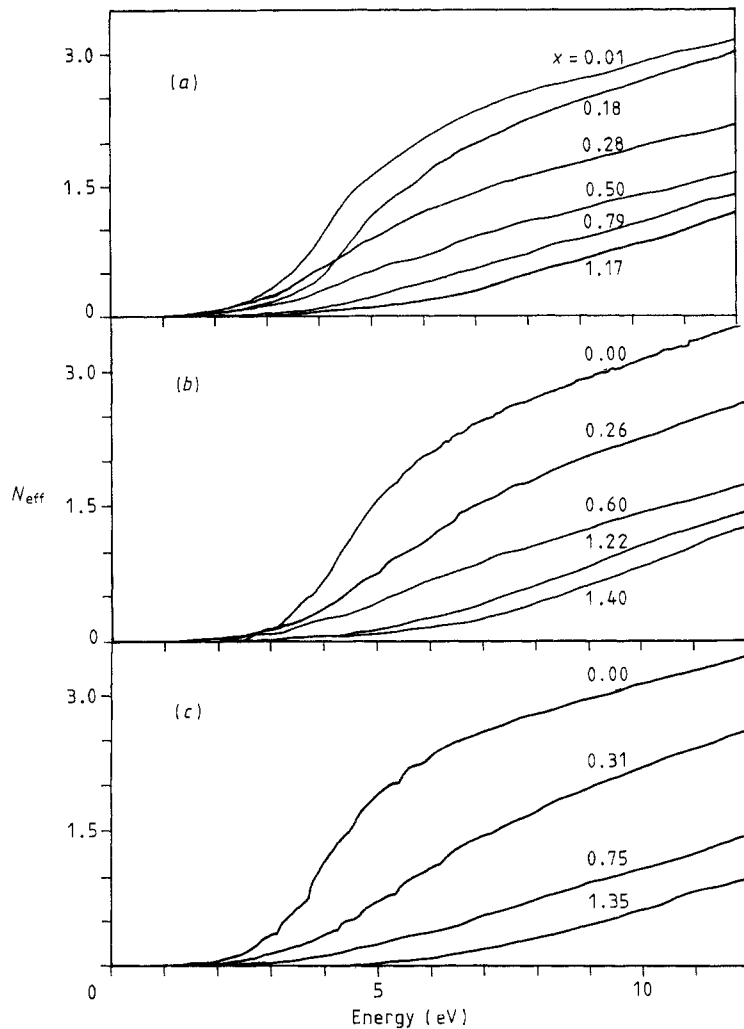


Figure 5. The effective number of electrons (n_{eff}) taking part in optical transitions up to an energy E for a-SiN_x (:H) films as a function of x . (a) Glow discharge; (b) sputtered (hydrogenated); (c) sputtered (no hydrogen).

uppermost three-peaked structure (in the centre of figure 8(a)) is predominantly derived from the N 2p states, with some states from Si 3p and 3s contributing respectively to the strengths of the lower two peaks in this group. The lower isolated peak is derived from N 2s and Si 3p states which happen to lie at the same energy. The conduction band (on the right-hand side of figure 8(a)) is formed from a mixture of N 2p, Si 3p and Si 3s anti-bonding states.

For SiN_x alloys, one could work out the relative contributions as a function of x to derive a JDOS and, from that, calculate the theoretical OJDOS or ϵ_2 -spectra. Fortunately, Martin-Moreno *et al* (1987) (MMVY) have provided ϵ_2 -spectra as a function of nitrogen content from their tight-binding calculations; we choose to compare our experimental spectra of ϵ_2 with their results, which are reproduced in figure 9.

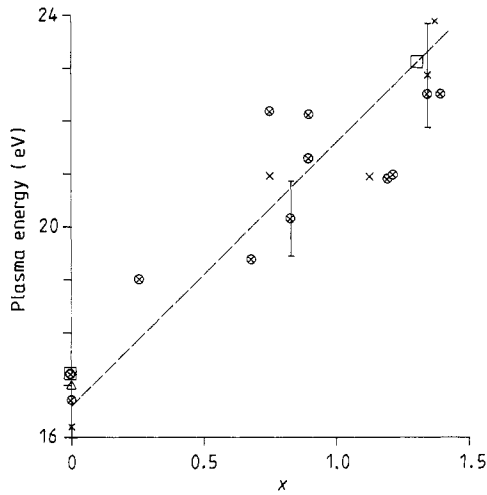


Figure 6. The plasma energy $E_p = \hbar\omega_p$ from core-level data as a function of nitrogen content x for films of $a\text{-SiN}_x(\text{:H})$: \otimes , sputtered, hydrogenated; \times , sputtered no hydrogen; \square , results of Nishijina and Fujimara (1977); Δ , result of Hezel and Lieske (1982).

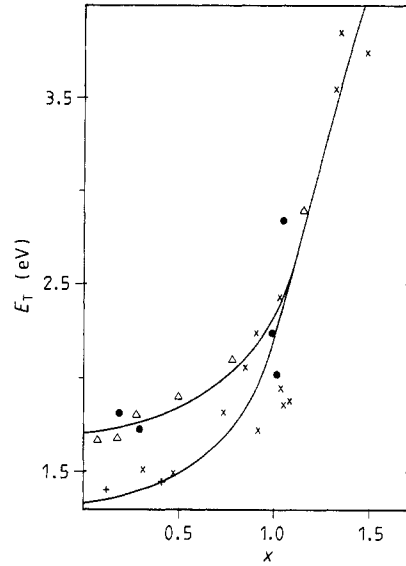


Figure 7. The Tauc optical gap E_T as a function of nitrogen content x for $a\text{-SiN}_x(\text{:H})$ films: Δ , glow discharge; $+$, sputtered (1 vol% hydrogen in plasma); \bullet , sputtered (3–6 vol% hydrogen in plasma); \times , sputtered (no hydrogen) (from Davis *et al* 1987).

First we consider the theoretical spectrum for $a\text{-Si}$ (top curve of figure 9). The large peak centred at about 3.5 eV and the smaller peak at about 7.5 eV arise, respectively, from transitions from the p- and s-like parts of the valence band to the conduction band. The first of these peaks matches well that seen experimentally for non-hydrogenated samples (figure 3(c)) in position, width and absolute height; the s-like peak, however, is not resolved experimentally, unless we consider the weak structure near 7 eV as indicating the possible presence of this feature. On increasing the nitrogen content, both the theoretical and experimental spectra display a shift of the main peak to higher energies, with the experimental peak moving somewhat more rapidly. At $x = 1$, i.e. for $a\text{-SiN}$, the theoretical curves begin to show evidence for nitrogen-derived states in the valence band, with features appearing at about 5 eV and 7–7.5 eV; these features reach full maturity at the stoichiometric composition $x = 1.33$. In contrast, our experimental curve for $x = 1.35$ exhibits no obvious structure that we can associate with transitions from nitrogen-derived states. However, the broad peak centred at ≈ 9 eV could be interpreted as representing the combined effect of nitrogen levels. Even in the theoretical curves, the separate features merge into one for higher x -values; according to MMVY this is due to interaction effects amongst first-neighbour lone-pair nitrogen states, which are expected to dominate at these high concentrations of nitrogen. They stress that their curves use only one adjustable parameter and refinements could no doubt be made to improve the fit to our data. Nevertheless, we consider the overall development of the theoretical and experimental spectra to be in good agreement.

It should be mentioned that nitrogen-derived peaks have been clearly seen in photoemission measurements by Karcher *et al* (1984), using both UV and x-ray excitation, at

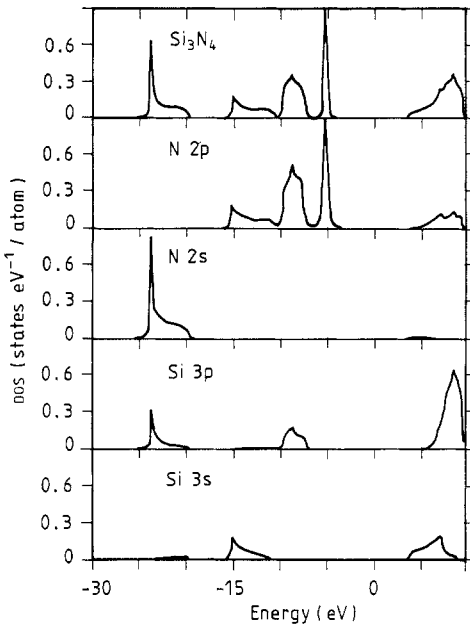


Figure 8. The DOS of Si_3N_4 and JDOS corresponding to Si- and N-derived states as calculated by Lucovsky and Lin (1985).

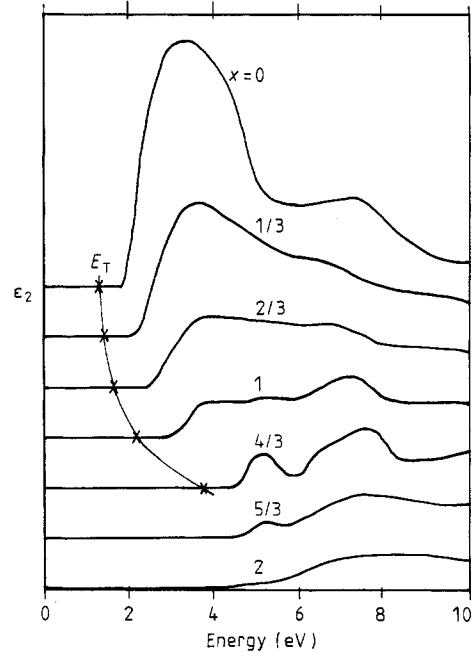


Figure 9. ϵ_2 -spectra for a- SiN_x as a function of x calculated by and reproduced from Martin-Moreno *et al* (1987). The curve on the left indicates the variation of E_T for unhydrogenated films (see figure 7).

4.9, 7.5 and 12.4 eV. The latter energy is beyond the limits of the theoretical curves and our own experimental data.

The shift of the threshold of the experimental ϵ_2 -spectra (and indeed the R -, ϵ_1 -, and OJDOS spectra) with increasing x is also well reproduced theoretically. The optical gap (to which the threshold corresponds) opens up dramatically as x approaches stoichiometry. The theoretical variation of the gap according to MMVY is somewhat faster than the experimental variation (figure 9), at least initially. MMVY predict a linear variation from ≈ 1.8 eV up to ≈ 3.5 eV just before $x = 1.33$ is reached; thereafter a rapid rise to ≈ 4.5 eV occurs. These authors ascribe the rapid rise to a decrease in the energy of the top valence band as Si-N bands take over from Si-Si bonds, whereas Karcher *et al* (1984) attribute it to an increase in the energy of the bottom of the conduction band. Spear *et al* (1987) propose a more or less symmetrical opening of the gap.

6. Conclusions

Reflectivity spectra have been obtained in the photon energy range 0.5–12 eV for amorphous films of SiN_x (:H) prepared by glow discharge and by sputtering (with and without hydrogen). The gross features of the spectra are independent of the method of preparation but they evolve continuously with increasing x .

From the reflectivity data, ϵ_1 , ϵ_2 , the OJDOS and n_{eff} have been obtained. The OJDOS spectra do not show any evidence for the emergence of discrete N-derived states in the

valence band. However, comparison of the ϵ_2 -data with theoretical spectra calculated using tight-binding methods indicates that, as stoichiometry is approached, the states at the top of the valence band change from Si- to N-related levels. The threshold of the spectra shifts to higher energies as x is increased and its variation agrees well with that of the Tauc gap determined by optical absorption edge measurements.

Acknowledgment

This work was supported by an SERC grant.

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