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Raman spectra of a-$Si_{1-x}N_x$:H films following natural ageing

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Abstract

The results are given of a comparison of vibrational spectra for a-Si_xN_{1-x}:H films on their natural ageing over the course of four years. The films of a-$Si_{1-x}N_x$:H with varying concentrations of NH_3, 2%, 4%, and 6%, were prepared from $NH_3 + SiH_4 + H_2$ gas mixture by plasma deposition. It is revealed that in the films containing 2% NH_3 in the mixture, there is crystallization with c-Si separation. However, with 6% and 10% of NH_3, the mixture stabilizes the amorphous state and does not influence the vibrational spectra and optical properties of the films. © 1997 Elsevier Science B.V.

Keywords: Raman spectra; Crystallization; Edge absorption; Natural ageing

1. Introduction

a-$Si_{1-x}N_x$:H films are interesting subjects for structural investigations [1] and are important materials for creating devices in micro- and optoelectronics [2,3]. For transistors [2,3] and quantum-dimensional structures [1] to operate continuously, the stability of the properties of components used in their manufacture is of special importance, particularly because at the glass–crystalline transition the parameters of a material can be changed by an order of magnitude [4]. Therefore, the investigation of the structure of a-$Si_{1-x}N_x$:H films is of great scientific and practical interest.

2. Experimental

The films of a-$Si_{1-x}N_x$:H under investigation were prepared from a $NH_3/H_2 + SiH_4 + NH_3$ gas mixture with 2%, 6% and 10% NH_3 by plasma deposition in a capacitive reactor system onto a Si substrate, with {111} orientation. The film thickness was 700–800 nm. To investigate the Raman spectra, an Ar-laser (λ_{ex} = 510 nm) and an He–Ne laser (λ_{ex} = 632,82 nm) with 2mW power were used. To measure Raman spectra, a DFS-24 spectrophotometer and a DILOR Z-24 spectrometer were used. IR spectra were taken using an IRS-29 spectrometer. The edge of optical absorption was investigated by conventional methods.

3. Results and discussion

Fig. 1 shows a Raman spectrum of a-$Si_{1-x}N_x$:H film based on 2% NH_3 taken in 1991. A similar spectrum of a-Si:H is given in Ref. [5]. The Raman spectrum in Fig. 1 consists of crystalline equivalence of phonons: TA at $\approx$ 150 cm^{-1}, TO $\approx$ at 480 cm^{-1}. The presence

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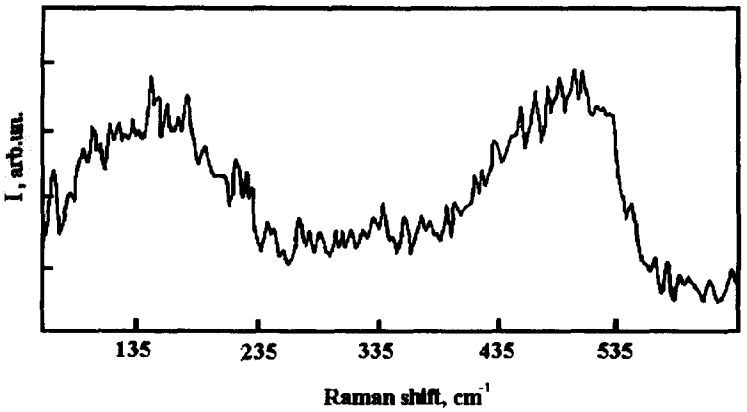

Fig. 1. Raman spectrum of a-$Si_{1-x}N_x$:H film based on 2% NH_3 measured in 1991.

of a band near 520 cm^{-1} in the Raman spectrum of the film with 2% NH_3 testifies to the formation of a small amount of crystalline phase in freshly evaporated a-Si:H film. A similar situation while preparing such films by the plasma deposition method was reported in Ref. [6]. The IR spectrum (Fig. 2, curve 2) indicates the formation of Si–N bonds in the film based on 2% NH_3 in which, with respect to the IR spectrum of pure a-Si:H, a wide band peculiar to Si–N bonds appears at 850 cm^{-1} [1]. On natural ageing for four years, marked changes take place in the structure of the film based on 2% NH_3; its Raman spectrum demonstrates this fact (Fig. 3, curve 2). In comparison with the Raman spectrum of freshly evaporated film (Fig. 1), the Raman spectrum of the film on natural ageing is considerably transformed and has an intense narrow band at 491 cm^{-1}. The shift of "the centre of weight" of the band to the localization of the LO vibrations of c-Si [7] and the considerable decrease in its half-width in comparison with the peculiarities of the Raman spectrum of freshly deposited film, testifies to the separation of c-Si crystalline phase in this film on natural ageing. Following natural ageing of the film based on 10% NH_3, its Raman spectrum differs slightly (Fig. 3, curve 1) from spectra of freshly evaporated films [7]. It is necessary to note that the absence of changes in the Raman spectra is also observed in the film based on 6% NH_3 in the mixture, with the same time of natural ageing (4 years). These spectra have a complex band with a large half-width having its maximum near 580 cm^{-1}. A joint consideration of the Raman and IR spectra of these films (Fig. 2, curves 1,4), (Fig. 3, curve 1) using published data [1,8] suggests a conclusion concerning the formation of Si–N bonds characteristic for the coordination of atoms, as in Si_3N_4 in the film based on 6 and 10% NH_3. The absence of any marked change in the vibrational

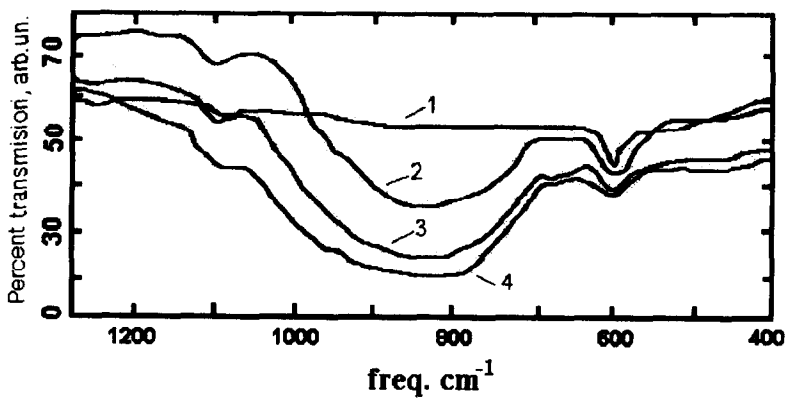

Fig. 2. IR spectra of a-$Si_{1-x}N_x$:H films with different contents of NH_3 in the mixture: 1, 0%; 2, 2%; 3, 6%; 4, 10%.

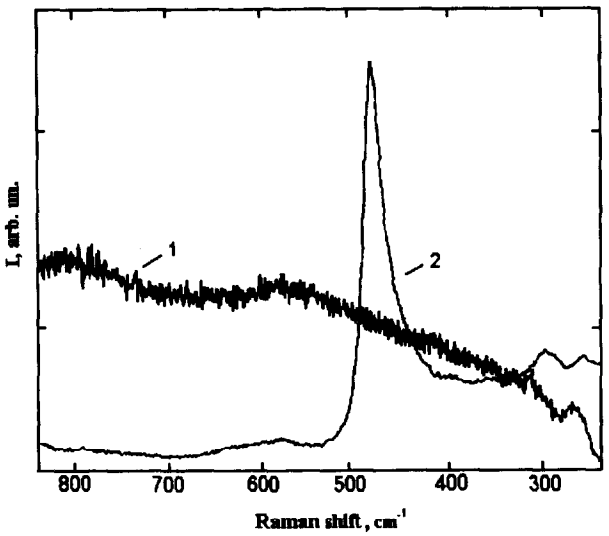

Fig. 3. Raman spectra of a-$Si_{1-x}N_x$:H films based on 10% (1) and 2% (2) contents of NH_3.

spectra of the film on natural ageing in comparison with freshly evaporated films suggests that 6% and 10% NH_3 in the mixture stabilizes the amorphous state. The absence of changes in the position of the absorption edge in the films with 6% and 10% NH_3 on natural ageing, supports this. However, in the film with 2% NH_3, the absorption edge shifts ΔE = + 0.1 eV to a high-energy region in comparison with its position in freshly deposited films. In this region, the absorption edge of c-Si is also present [9].

4. Conclusion

On natural ageing over four years of a-$Si_{1-x}N_x$:H films based on 2% of NH_3, crystallization with c-Si separation occurs. Increase in the NH_3 content up to 6% and 10% in the mixture stabilizes the amorphous state of a-$Si_{1-x}N_x$:H films and does not influence their vibrational spectra and optical properties.

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