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CONCENTRATION PROFILES OF ELEMENTS AND STRUCTURE OF a-$Si_{1-x}N_x$:H FILMS

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SIMS profiles of a-$Si_{1-x}N_x$:H films having different composition have been measured. The distribution of hydrogen in nitrided films bears a fluctuating character and its whole content decreases at $x < 0.06$. In all films, Na impurity is observed and its content on the film surface exceeds that of all other components. In the region of small contents of nitrogen, the position of the absorption edge in a-$Si_{1-x}N_x$:H films does not change with respect to its position in a-Si:H. According to the analysis of IR spectra of a-$Si_{1-x}N_x$:H near Si-N bonds, different surroundings are realized.

1. Introduction

It has been established that adding nitrogen carbon into a-Si:H film causes the change in the microstructure and electrophysical properties of a-$Si_{1-x}N(C)_x$:H films [1-3].

The perspectives of using nitrided films for the production of opto- and microelectronic devices require [4] the information on the chemical element distribution over the thickness of such films that are prepared on Si substrates and the relation to their structure and optical properties. By changing the concentration of nitrogen in the material, one can control the value of band gap and the density of defects [5]. The investigation of features of the nitrogen distribution in the a-Si:H films may seem useful for creating the structure of nitrided films [6,7].

In the present article, the results of studies of a-$Si_{1-x}N_x$:H films SIMS profiles and the data on their vibrational spectra and optical absorption edge are given.

2. Experimental procedure

The investigated films were prepared by plasma discharge deposition of the R = $NH_3/(H_2+SiH_4+NH_3)$ mixture containing 0, 2, 6, or 10% of NH_3. The parameters were as follows: substrate temperature $T = 220°C$, discharge power of 0.3 W/cm^2 (at the frequency of 13.56 MHz), total pressure of 50 Pa (0.37 Torr) and flow rate of 100 cm^3/min. The element distribution profile over the film thickness was measured by second-ion mass spectrometry method with O^+-ion etching, using the Cameca IMS4F instrument. The IR absorption (400 to 1400 cm^{-1}) was measured by the spectrophotometer IRS-29. The band gap (E_0) of the films was defined at the level of $a = 10^4$ cm^{-1}. All films had nearly equal thickness of 700 to 800 nm.

3. Results and discussion

Figure 1 shows the depth dependence of Si, N, H and Na distribution over the thickness of a-$Si_{1-x}N_x$:H ($x = 0$) film. The distribution of hydrogen suffers insignificant deviations from a constant value over the entire film thickness. The signal intensity due to Na impurity exceeds the signal intensity due to other elements, whereas in the central part the intensities of Na and N impurities are comparable.

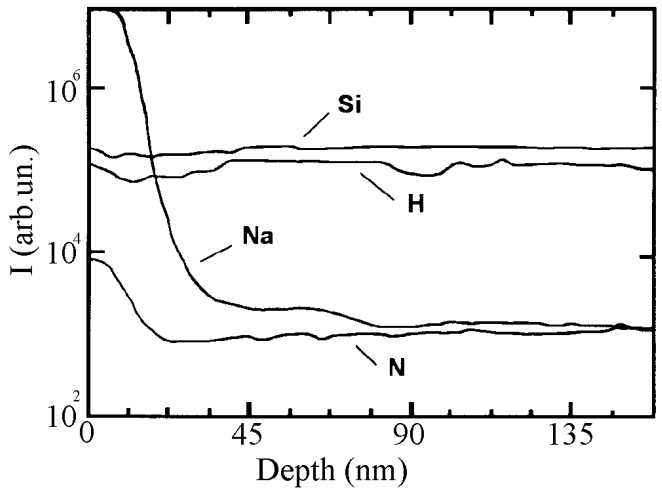

Fig. 1. SIMS profiles of a-Si:H film.

In the a-$Si_{1-x}N_x$:H film based on 2% of NH_3 in the mixture (Fig. 2), the content of hydrogen over the film thickness is lower than in the a-Si:H (Fig. 1), and the distribution bears a fluctuating character. It increases gradually when going from the film surface.

Si content decreases a little while going from the film surface. The availability of Na impurities in their composition is common for all films which were investigated. Moreover, in the near-surface region, the concentration of Na is very high. The fixing of Na ions in SIMS spectra is expected. According to Ref. 8, we know that in the process of oxidation of SiO_2 from O_2+2(H_2O), easily mobile Na ions are always present in SiO_2 film which worsen the parameters of electronic devices based on them. To reduce the influence of this factor on the characteristics of the devices, HCl was usually added to O_2+2(H_2O) that caused the formation of Na, bonded into NaCl, on the substrate. Thus, the characteristics of the devices are essentially stabilized due to the absence of drift of Na ions in strong electric fields.

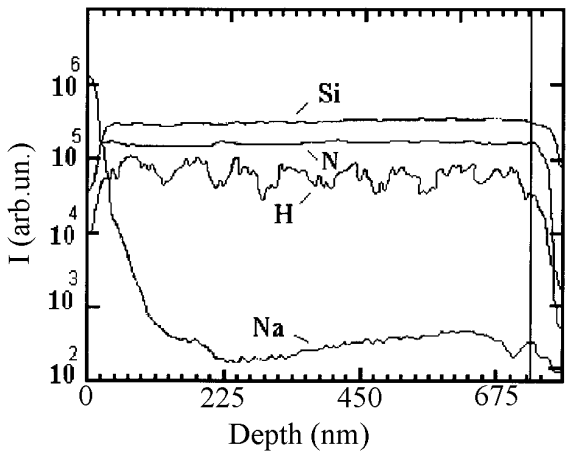

Fig. 2. SIMS profiles of a-$Si_{1-x}N_x$:H film at the NH_3 concentration in the mixture of 2%.

With further increase of NH_3 in the mixture to 6%, the concentration of nitrogen in the film increases as expected (Fig. 3). The whole SIMS profile does not suffer deviation from a straight line. Judging by the signal intensity of hydrogen ion its content in the film based on 6% NH_3 is higher than that based on 2% NH_3. However, in both cases the distribution of hydrogen over the film thickness bears a fluctuating character. In the film with 10% of NH_3, the concentration of hydrogen remains the same as in the film with 6% of NH_3, and the fluctuation over the thickness becomes less pronounced.

Estimation of the average etching rate (V_e) of films by O^+-ions showed that when the concentration of NH_3 in the mixture is 0, 2 and 6 %, $V_e = 2.2 - 2.3$ nm/min, whereas in the case of the film based on 10 % of NH_3 V_e, it is almost twice as large.

According to the analysis of IR spectra (see Fig. 4), nitriding of a-Si:H causes the formation of Si:N bonds. The increase of the intensity at the "weighted centre" near 850 cm^{-1} is a direct evidence to this fact. A similar band was observed in a-$Si_xN_yH_z$ films [9].

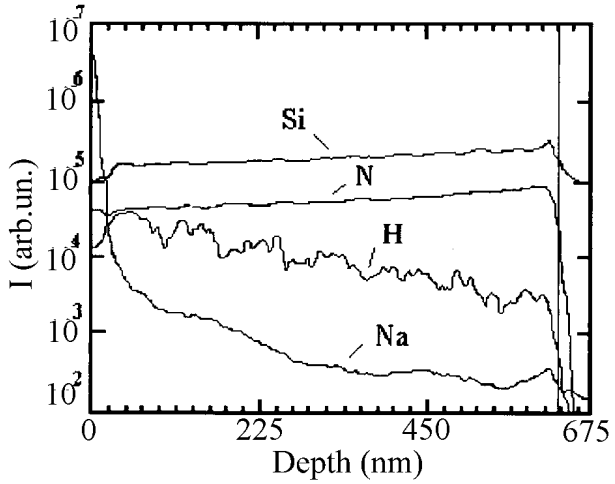

Fig. 3. SIMS profiles of a-$Si_{1-x}N_x$:H film at the NH_3 concentration in the mixture of 6%.

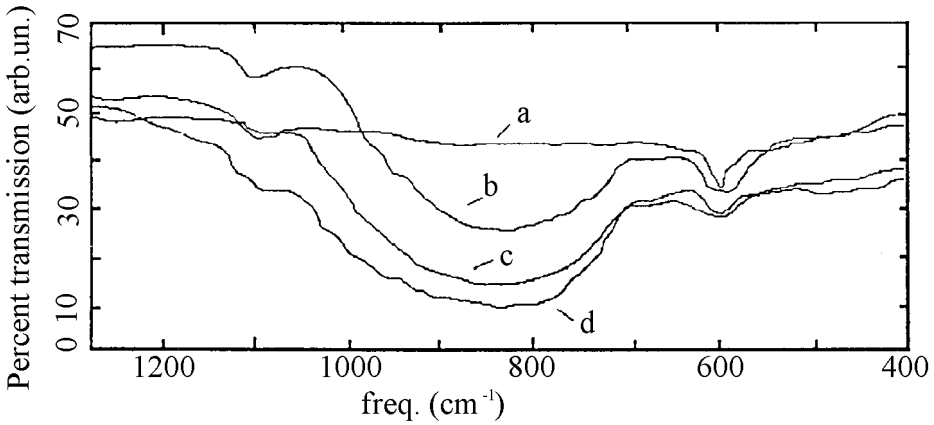

Fig. 4. IR absorption coefficients of a-$Si_{1-x}N_x$ films for different concentrations of NH_3 in the mixture: a) 0%, b) 2%, c) 6% and d) 10%.

Adding a small quantity of N ($x < 0.06$) results in structure homogenization of the material, whereas the increase in N content is again accompanied by the formation of grains with a well-pronounced structure of boundaries [2].

According to Ref. 9, a large half-width of bands in IR spectra of a-$Si_{1-x}N_x$:H films may be assigned to the availability of different surroundings near the Si-N bond. It is considered that if the second neighbour of nitrogen through Si is Si only, then the shoulder near 790 cm^{-1} appears, and the band at 850 cm^{-1} is characteristic for nitrogen whose

second neighbour through Si is hydrogen. The characteristic bands near 3300 and 2100 cm^{-1} indicate to the formation of N-H and Si-H bonds, respectively [9].

A band of weak intensity near 1100 cm^{-1} is usually observed in IR spectra of films coated with SiO_2 thin layer.

The formation of new bands connected with nitriding a-Si:H influences the position of the absorption edge (Fig. 5). However, if $R \leq 0.01$, the band gap E_0 and the refractive index of the film with 2% of NH_3 differ very little from the value for a-Si:H film (see Table 1). At $R > 0.1$, the absorption edge of a-$Si_{1-x}N_x$:H films shifts to a high-energy region.

TABLE 1. Positions of absorption edges and refraction indices of a-$Si_{1-x}N_x$:H films.

Parameters	Concentration of NH_3 in the mixture			
	0%	2%	6%	10%
E_0 (eV)	2.05	2.04	2.29	3.08
n	3.7	3.6	2.7	2.3

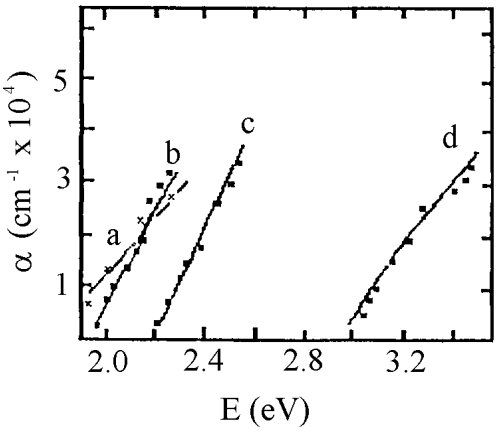

Fig. 5. Absorption edges in a-$Si_{1-x}N_x$:H films for different concentrations of NH_3 in the mixture: a) 0%, b) 2%, c) 6% and d) 10%.

Considering the results of studies of SIMS profiles, of optical properties and of earlier data from electro-microscopic studies [1–3], one can conclude that small addition of nitrogen, $x < 0.06$, in a-$Si_{1-x}N_x$:H films causes the decrease in the entire content of hydrogen, replacement of Si-H bonds by more stable N-H bonds and homogenization of the structure in the bulk of the material. Further increase in the content of nitrogen ($x > 0.06$) is accompanied by the formation of Si nitride complex that leads to a marked change in optical characteristics of the films ($E_0 = 3.08$ eV, $n = 2.3$) and of their microstructure.

4. Conclusions

Small amount of nitrogen in a-$Si_{1-x}N_x$:H thin films for $x < 0.06$ does not essentially change the short-range order and the optical characteristics of the films. The distribution of hydrogen in all nitrided films fluctuates over the thickness. At $x > 0.06$, a considerable transformation of the short-range order in a-$Si_{1-x}N_x$:H films is observed and the optical characteristics of the films change to a considerable extent.

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KONCENTRACIJSKI PROFILI ELEMENATA I STRUKTURA TANKIH SLOJEVA a-$Si_{1-x}N_x$:H

Proučavali su se SIMS profili tankih slojeva a-$Si_{1-x}N_x$:H različitih sastava. Raspodjela vodika u nitriranim slojevima je promjenljiva i njegov sadržaj opada za $x < 0,06$. U svim se uzorcima opazilo onečišćenje natrijem koje na površinama slojeva nadmašuje sva druga onečišćenja. Za male dodatke dušika se položaj apsorp- cijskog ruba u slojevima a-$Si_{1-x}N_x$:H malo mijenja u odnosu na a-Si:H. Prema analizama IR spektara a-$Si_{1-x}N_x$:H oko Si-N vezanja, ostvaruju se različiti atomi oko Si atoma u slojevima.