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Phase Transformation in the Annealed Si-Rich SiN_x Films Studied by Raman Scattering

F.F. Komarov[1,*], L.A. Vlasukova[1], I.N. Parkhomenko[1], O.V. Milchanin[1], A.K. Togambaeva[2], S.Yu. Udovichenko[3], K.V. Misiyuk[3]

[1] *Belarusian State University, 4, Nezavisimosty Ave., 220030 Minsk, Belarus*
[2] *Al-Farabi Kazakh National University, 71, Al-Farabi Ave., 050038 Almaty, Kazakhstan*
[3] *Tyumen State University, 23, Lenina Ave., 625003 Tyumen, Russia*

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The Si-rich SiN_x films were deposited on Si wafers by low pressure chemical vapor deposition (LPCVD) technique followed by annealing at (800-1200) °C. Excess (overstoichiometric) Si content in nitride films was calculated from Rutherford backscattering data (RBS). Existence and evolution of Si nanoclusters from amorphous to crystalline ones under high temperature treatment were confirmed by Raman scattering (RS) measurements. Amorphous Si clusters have already existed in as-deposited SiN_x films. Thermal treatment results in the formation of additional amorphous nanoclusters and in their crystallization with anneal temperature increasing. Nitride films annealed at 1200 °C contain crystalline Si clusters only. It was revealed a dependence of Si wafer's Raman scattering intensity on the temperature of SiN_x/Si structures annealing. This information in combination with RBS data has allowed us to estimate and distinguish the excess silicon aggregated in clusters and the excess silicon distributed over the silicon nitride matrix.

Keywords: Si-rich silicon nitride, Low-pressure chemical vapor deposition, Annealing, Rutherford backscattering, Raman scattering.

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1. INTRODUCTION

A great deal of interest has been devoted recently to silicon nanocrystals embedded in dielectric matrix due to its potential application in nanoelectronics and optoelectronics. The most preferred matrix for silicon nanocrystals is silicon nitride because of its low barrier high charge trapping capacity and high carrier mobility.

Compared with other conventional methods using to study nanocrystals such as transmission electron microscopy and X-ray diffraction, micro-Raman scattering (RS) spectroscopy is much preferred for its nondestructive measuring, small specimen quantity and short measurement time. The aim of this research is to study phase transformations including formation and crystallization of Si clusters in Si-rich SiN_x films under high temperature treatment.

2. EXPERIMENTAL

The Si-rich SiN_x films were deposited on n-type (100)-oriented Si substrates by low-pressure chemical vapor deposition (LPCVD) technique using a gaseous mixture of dichlorosilane (SiH_2Cl_2) and ammonia (NH_3) as precursors. The deposition temperature was 800 °C. The thickness and refractive index of nitride films were measured by ellipsometry at $\lambda = 632.8$ nm. Two SiN_x/Si wafers denoted B1 and B2 were taken. Table 1 shows the values of thickness and refractive index of as-deposited nitride films for B1 and B2.

Afterwards, the samples with the size of 1×1 cm^2 were cut from B1 and B2 and annealed at 800 °C and 1000 °C for 60 min using resistance furnace and at 1200 °C for 3 min using rapid thermal annealing (RTA) setup 'jetFirst'. The depth distribution of Si and N atoms in as-deposited SiN_x films were analyzed by Rutherford backscattering spectrometry (RBS) using 1.3 MeV He^+ ions.

Table 1 – Characteristics of as-deposited SiN_x films

Samples	Refractive index n	Thickness, nm
B1	2.2	850
B2	2.2	950

The structural properties of Si nanoclusters in as-deposited and annealed SRSN films were studied using Raman scattering technique. RS measurements were carried out by micro-Raman setup Nanofinder with an exciting wavelength of 473 nm at room temperature in back-scattering geometry.

3. RESULTS AND DISCUSSION

It is known that ratio of Si/N atoms is equal to 0.75 for stoichiometric silicon nitride Si_3N_4. It corresponds to 42.86 at.% Si and 57.14 at.% N. Rutherford backscattering data show the concentration of Si in the sample B1 is (69-72%). The concentration of Si atoms in the sample B2 is (65-50%). Thus, both investigated samples are Si-rich silicon nitride films. The silicon nitride in the sample B1 contains more Si atoms than the sample B2.

Fig 1 shows Raman spectra of the as-deposited and annealed at (800 – 1200 °C) samples B1 and B2.

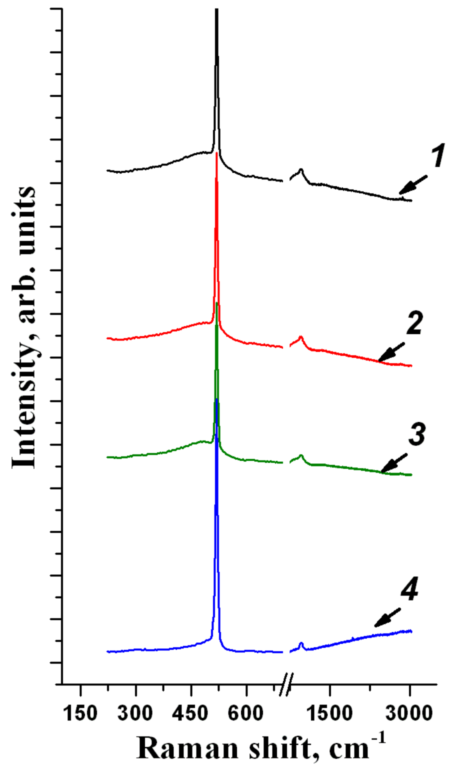
The narrow peak at 520 cm^{-1} is observed in all Raman spectra. It arises from the scattering by Si (100) substrate. The Raman spectra of the both as-deposited samples contain broad band at 480 cm^{-1}. This band is typical of amorphous silicon [1]. Thus we can conclude

* komarovF@bsu.by

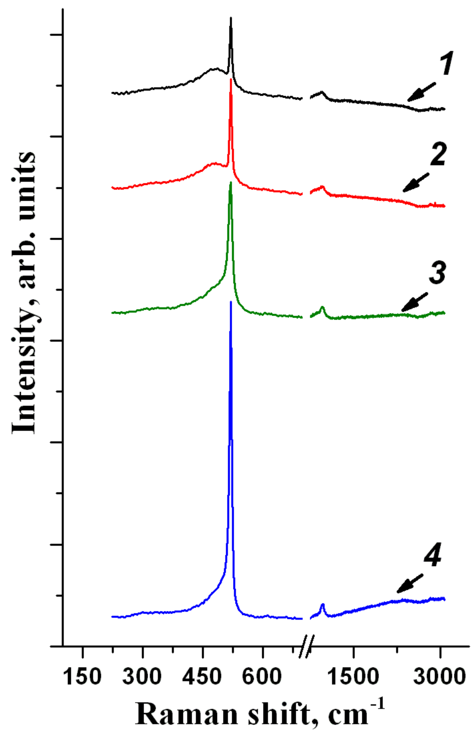
that amorphous silicon clusters present in both as-deposited samples.

An analysis of RS spectra transformation with annealing temperature reveals two similar features for the both sets of samples under investigation. The first one is a disappearance of the band at 480 cm^{-1} with the growth of annealing temperature and an appearance of the low-energy tail of the band at 520 cm^{-1}. We suggest that low-energy tail is attributed to the scattering from silicon nanocrystals. Similar modifications of Raman spectra were observed in ref [2] for Si-rich silicon oxide films with embedded Si nanoparticles. In this article, the RS spectra of the SiO_x films annealed at 1300 K for 60 min exhibit two components. The sharp peak was assigned to the silicon substrate. A low-energy tail was due to Si nanocrystals. The presence of Si nanocrystals was confirmed in [2] by high resolution electron microscopy. Thus, the spectral transformations in Fig. 1 can be assigned to crystallization of amorphous clusters in the films. It should be noted, that in the case of B2 the low-energy tail appears after annealing at lower temperature (1000 °C) in comparison with B1. As regards the sample B1, the band at 480 cm^{-1} vanishes and weak low-energy tail appears only after annealing at 1200 °C. One can conclude that the temperature of amorphous clusters crystallization is different for the samples B1 and B2. It can be caused by the difference between an average size of initial amorphous clusters embedded in the as-deposited films B1 and B2. The size dependent crystallization temperature of silicon nanocrystals was studied by means of the RS measurements in Ref. [3]. According to Ref [3], the temperature threshold of the transition amorphous/crystalline silicon nanoclusters decreased as the particle size decreased. Thus, one can conclude the average size of silicon clusters in the sample B1 is larger than in the sample B2. It doesn't contradict the higher excess silicon content in the sample B1.

The second similar feature of RS spectra of two sets of samples is a dependence of the intensity of narrow "substrate" band at 520 cm^{-1} on annealing temperature. Usually, the scattering from Si substrate is undesirable in the RS measurements of SRSN films. A strong signal from monocrystalline Si at 520 cm^{-1} prevents the observation of weaker bands of amorphous and crystalline precipitates in the region of (450 – 520 cm^{-1}). Though, one can get useful information about phase composition of the nitride films from the analysis of the intensity of "substrate" peak at 520 cm^{-1} with the annealing temperature growth. Fig. 2 shows the intensity of 520 cm^{-1} "substrate" band as function of the annealing temperature for the both sets of samples. The intensity of this peak significantly increases after annealing at 1200 °C for the both B1 and B2 samples. It can be explained by restoration of silicon nitride host matrix via the annealing of the structural defects. On the other hand, crystallization of Si clusters can results in increasing of intensity at 520 cm^{-1}. Inset in fig. 2 shows the absorption spectra of crystalline and amorphous silicon presented in ref. [4]. The vertical line at 473 nm in the inset indicates the exciting laser line in our RS measurements. As can be seen the absorption at the 473 nm in amorphous Si is stronger than in crystalline Si. Therefore the transmission of the SiN_x layer with crystalline Si clusters should be higher in comparison with the SiN_x layer contained amorphous clusters.



a



b

Fig. 1 – The Raman spectra of as-deposited (curve 1) and annealed at 800 °C (curve 2), 1000 °C (curve 3) and 1200 °C (curve 4) samples B1 (a) and B2 (b)

It is obvious, as the top layer become more transparent, as the scattering from the substrate increases. The annealing at 1200 °C results in formation of crystalline clusters in both samples. Thus the significant increasing of the intensity of 520 cm^{-1} band after annealing at 1200 °C can be explained by crystallization of initial amorphous Si clusters.

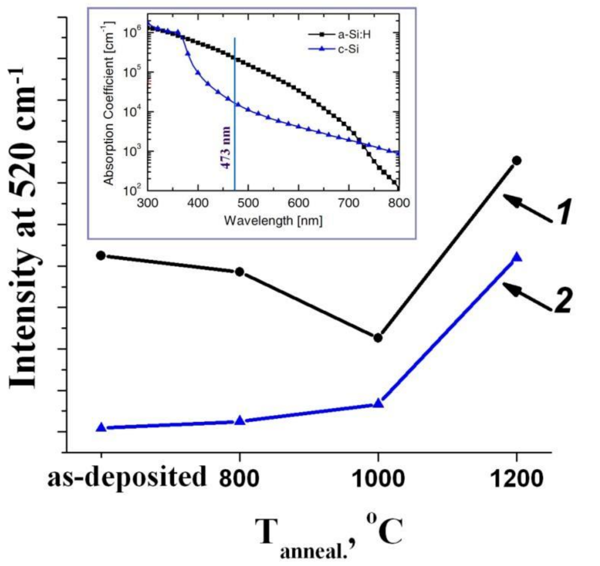


Fig. 2 – The RS intensity of the band at 520 cm^{-1} from Si substrate as function of annealing temperature for B1 (curve 1) and B2 (curve 2). The inset shows the absorption spectra of the crystal and amorphous silicon from Ref. [4].The vertical line indicates the exciting laser line in our RS measurements.

However, there is difference between two curves in Fig. 2. With the growth of annealing temperature to 1000 °C, the intensity of the peak at 520 cm^{-1} increased for B2 and decreased for B1. As mentioned above, the both as-deposited samples contain amorphous clusters. It should be noted, that the intensities of band at 480 cm^{-1} originated from the amorphous Si clusters are similar for both as-deposited samples. One can suggest that the amounts of excess silicon in clusters are similar in both as-deposited samples. On the other side, RBS data demonstrate higher excess silicon content for B1 in comparison of B2. Hence, the amount of excess Si atoms distributed randomly in the SiN_x matrix is higher in B1. Volodin *et al.* [5] observed increasing of absorption of SiN_x (x<1) films at the range of 250 – 500 nm after furnace annealing at 1130 °C for 5 h in Ar ambient. The increase of SiN_x layer absorption was explained by a formation of amorphous Si clusters from excess silicon atoms distributed in the SiN_x matrix. In our case the formation of amorphous clusters can result in growth of SiN_x layer absorption, too. As a result, the transmission of the top SiN_x layer and scattering by the Si substrate should decrease. Besides, as mentioned above, clusters in the as-deposited sample B1 are too large to crystalize under annealing at 800 - 1000°C. Thus insufficient annealing temperature for crystallization of amorphous clusters and formation new amorphous Si clusters during annealing at 800 – 1000 °C can result in decreasing scattering by the substrate for the sample B1. On contrary, there are smaller Si clusters which begin crystallize at lower temperature in the sample B2. Besides, the analysis of RBS and RS data shows that as-deposited B2 contains less excess Si atoms distributed over SiN_x matrix than B1. Therefore, in B2 the intensity of peak at 520 cm^{-1} slowly increases with the increasing of annealing temperature in the range of 800 – 1000°C due to crystallization of small initially amorphous clusters.

4. CONCLUSIONS

The Si-rich SiN_x films were deposited on Si wafers by low pressure chemical vapor deposition technique followed by annealing at (800 – 1200) °C. Two sets of as-deposited and annealed nitride films named as B1 and B2 were investigated with Rutherford backscattering and Raman scattering. As-deposited SiN_x films from two sets were characterized with the same refractive index (2.2) and the similar thickness (850 nm for B1 and 950 nm for B2). RBS data show that the both samples are Si-rich silicon nitride, but the sample B1 contains more excess (overstoichiometric) Si atoms than the sample B2.

From Raman scattering data it was found that amorphous Si clusters already existed in as-deposited SiN_x films for the both sets of samples. Annealing results in the formation of additional amorphous nanoclusters and in their crystallization with the growth of anneal temperature. After annealing at 1200 °C nitride films from the both sets contained crystalline Si clusters only. According to the RS data the nitride film with higher excess Si (B1) contained larger silicon nanocrystals in comparison with the sample B2.

It was revealed a dependence of Raman scattering intensity from Si wafer on the temperature of SiN_x/Si structures annealing. This information in combination with RBS data allowed us to estimate and distinguish the excess silicon aggregated in clusters and distributed over the silicon nitride matrix. We suggested that in the case of nitride film with higher excess Si (B1) some quantity of excess Si was remained in nitride matrix as randomly distributed Si atoms in atomic network, not as Si nanocrystals, even after annealing at 1200 °C. In the case of nitride film with lesser excess Si (B2) practically all excess Si was aggregated into Si nanocrystals after annealing at 1200 °C.

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