

# Raman study of silicon nanocrystals formed in SiN<sub>x</sub> films by excimer laser or thermal annealing

V. A. Volodin, M. D. Efremov,<sup>a)</sup> V. A. Gritsenko, and S. A. Kochubei

*Institute of Semiconductor Physics SB RAS, Novosibirsk 630090, pr.ak.Lavrentjeva 13, Russia*

(Received 21 January 1998; accepted for publication 24 June 1998)

Silicon nitride films of different stoichiometric composition were studied using Raman spectroscopy. A Raman signal due to Si–Si, Si–N bond vibrations in silicon nanoclusters was detected in as-deposited films. The appearance of Raman peaks in the range 493–514 cm<sup>-1</sup> after thermal and pulse laser treatments was interpreted as formation of silicon nanocrystals with sizes from 1.3 up to 5 nm depending on treatment parameters. Thermal treatment at 1200 °C allowed Si atom diffusion and its gathering in Si nanocrystals, meanwhile 5 ns pulse laser irradiation leads to crystallization of preexisting silicon nanoclusters inside the as-deposited SiN<sub>x</sub> films. © 1998 American Institute of Physics. [S0003-6951(98)03334-8]

At present, the interest in research of optical properties of silicon nanocrystals (SNs) in wide-band-gap materials has been aroused by its possible applications in silicon-based integrated optoelectronic devices. Among these properties, the high intensive room-temperature luminescence originated due to confinement of electrons and holes in the SNs seems the most important. The possibility to control the luminescence varying the SN sizes is of special interest. Much effort has been devoted to research of the optical properties of SNs in silicon oxide films, whereas silicon nitride films may have some advantages. It is well known that barriers at the Si/SiO<sub>2</sub> interface are 3.8 and 3.15 eV for holes and electrons, respectively, which requires the large electric fields to inject electrons and holes into the oxide. In this case the electric fields became comparable with the breakdown value for SiO<sub>2</sub>. In the case of the Si/Si<sub>3</sub>N<sub>4</sub> interface the barriers are 2.0 and 1.5 eV for electrons and holes, accordingly, which provides more beneficial conditions for carrier injection. In this work an attempt to create SNs in silicon nitride was realized using thermal and pulsed laser treatments of SiN<sub>x</sub> films with different excesses of silicon atoms.

The studies SiN<sub>x</sub> films of different compositions were deposited using a low-pressure chemical vapor deposition technique on silicon(001) substrates from a SiH<sub>2</sub>Cl<sub>2</sub> and NH<sub>3</sub> mixture at 760 °C. Three kinds of samples with various compositions were manufactured. Data concerning these films are shown in Table I, where *R* is the SiH<sub>2</sub>Cl<sub>2</sub>/NH<sub>3</sub> ratio, *d* is the thickness of the films, *x* is the atomic ratio of nitrogen to silicon, and *n* is the refractive index of the films for light with a wavelength 633 nm. Then, the films were treated by radiation of a 5 ns pulse XeCl excimer laser (EL) with a wavelength of 308 nm or by a 2 h furnace annealing in Ar atmosphere at 1200 °C (see Table I). The structural properties of as-deposited and annealed films were studied using Raman spectroscopy. All Raman spectra were recorded in quasibackscattering geometry at room temperature using a double spectrometer equipped with a cooled photon-counting device. The 488 nm argon laser line was used for excitation of scattering.

There is translation symmetry in crystals and the law of conservation of momentum has to be satisfied, so, for scattering photons in the visible range (the wave vector is about three orders of magnitude smaller than the Brillouin zone), longitudinal optical (LO) and transverse optical (TO) phonons with very small wave vectors are active in single-particle scattering. For silicon without mechanical stress these modes are degenerated and have a frequency 520 cm<sup>-1</sup>, so, Raman spectra of monocrystal Si are characterized by a narrow peak at this position. In the case of a (001)-oriented silicon surface, according to symmetry selection rules, only LO modes are active for backscattering geometry. The Raman tensor for LO modes is

$$\begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

There is no translation symmetry in amorphous solids, therefore, the law of conservation of momentum vanishes, and Raman spectrum of amorphous silicon is characterized by the density of phonon states, which has a broad maximum near 480 cm<sup>-1</sup>. The Raman spectrum of SN is characterized by peaks resulting from scattering on optical phonon modes localized in the nanocrystal. The position and the width of the peaks strongly depend on the size and structure of the nanocrystal according to dispersion of localized modes. Its position approximates to 520 cm<sup>-1</sup> when the size of the crystal cluster grows up. So, Raman spectroscopy allows us to obtain information about the presence of nano- and micro-clusters of crystal silicon in various surroundings and also about their size dispersion.<sup>1-3</sup>

TABLE I. Specification of the studied samples.

Parameters of films and treatments:	<i>R</i> =0.5	<i>R</i> =1.3	<i>R</i> =1.6
	<i>d</i> =2000 Å <i>x</i> =1.3 <i>n</i> =2.0	<i>d</i> =2000 Å <i>x</i> =1.2 <i>n</i> =2.1	<i>d</i> =3000 Å <i>x</i> =0.85 <i>n</i> =2.4
As-deposited film	A	B	C
EL, 300, 260 mJ/cm <sup>2</sup>		BE	CE
TA, 1200 °C, 2h		BT	CT

<sup>a)</sup>Electronic mail: efremov@isp.nsc.ru

TABLE II. Parameters of the observed Raman peaks.

Film	Peak	Center cm <sup>-1</sup>	Width cm <sup>-1</sup>	Intensity a.u.
A	A1	429	23	26
B	B1	483	8	8
	B2	422	37	16
	C1	493	34	57
C	C2	470	21	38
	C3	440	35	51
BE	BE1	512	7	10
	BE2	464	87	21
	CE1	508	12	26
CE	CE2	493	13	29
	CE3	473	34	44
	CE4	443	10	16
	BT	BT1	506	24
BT	BT2	483	8	3
	CT1	514	7.5	7
CT	CT2	501	12.5	8
	CT3	487	6	3

Because the studied films were semitransparent for the wavelength of excited light, the polarization geometry of scattering was chosen to eliminate very intensive peaks caused by scattering on long-wave LO phonons in the Si(001) substrate. The geometry used was  $Z(XX)\bar{Z}$ , where  $Z$  (the direction of the photon impulse) and  $X$  (the direction of the photon polarization) are the (001) and (100) directions, correspondingly. In this geometry scattering on long-wave LO phonons in the monocrystal Si(001) substrate is forbidden, but for nanocrystals with random orientation the scattering on localized optic phonon modes is allowed.

Table II contains characteristics of peaks observed in the Raman spectra of as-deposited and treated films. Peak position, width, and amplitude were obtained from correspondent Lorentz curves fitted to the experimental ones.

Raman spectra of as-deposited  $\text{SiN}_x$  films of different composition are shown in Fig. 1. The narrow peak at 520 cm<sup>-1</sup> observed in all spectra corresponds to scattering by the silicon substrate (in spite of the forbidden geometry, probably due to the imperfect backscattering in the real experiment or due to defects in the substrate) and is related with scattering on the LO long-wave phonon modes in monocrystal

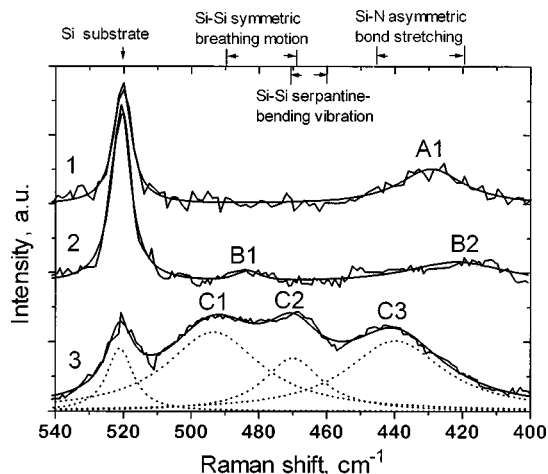


FIG. 1. Raman spectra of samples with various excesses of Si atoms: 1,  $x = 1.3$ ; and 2,  $x = 1.2$ ; 3,  $x = 0.85$ .

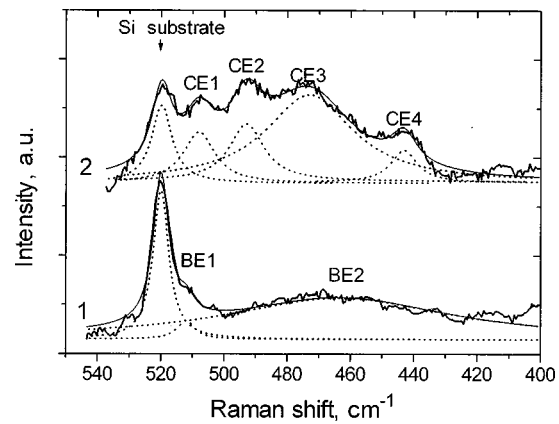


FIG. 2. Raman spectra of  $\text{SiN}_x$  films after EL annealing with: 1,  $x = 1.2$ , energy density 300 mJ/cm<sup>2</sup>; and 2,  $x = 0.85$ , energy density 260 mJ/cm<sup>2</sup>.

tal Si, because, as it was mentioned above, the films were very thin and semitransparent for excited light. In the samples with a comparatively low excess of silicon ( $x \geq 1.2$ ), the signal due to scattering on Si-Si bonds (broad maximum near 480 cm<sup>-1</sup> corresponding to the density of states of local TC-like phonon modes in amorphous silicon) are not detected. Obviously, it is connected to the low concentration of such bonds in silicon nitride with low Si atom excess. For sample 3 ( $x = 0.85$ ) the Raman peaks associated with excessive Si atoms are clearly seen. Two features (C1-493 cm<sup>-1</sup> and C2-470 cm<sup>-1</sup>, Fig. 1, Table II) could be related to scattering on Si-Si bond vibrations with the possible contribution of different modes: scissors-bending vibration (frequency range 450–465 cm<sup>-1</sup>), serpentine-bending vibration (460–470 cm<sup>-1</sup>) and symmetric breathing motion (470–490 cm<sup>-1</sup>) of the Si-Si bonds in a cluster composed of eight silicon atoms in the surrounding nitrogen.<sup>4</sup> But, the position of peak C1 is somewhat higher in the energy range as compared with the calculated frequency of the above-mentioned local vibration of Si-Si bonds.<sup>4</sup> So, one may propose that the peak C1 can correspond to scattering on optic phonons localized in very small nanoclusters (about 1.3 nm according to our estimates). Peak C3 observed in spectrum 3 (Fig. 1) at a region of nearly 440 cm<sup>-1</sup> can be connected with the scattering on the asymmetric Si-N bond stretching mode<sup>4</sup> in the above-mentioned cluster with one neighbor Si atom removed and one central Si atom substituted by a N atom. For samples with a low excess of silicon (spectra 1,2 in Fig. 1), very small peaks A1 and B2 could be connected with scattering on Si-N bonds.

In Fig. 2 the Raman spectra of samples with  $x = 1.2$  after the excimer laser treatment with an energy density 300 mJ/cm<sup>2</sup> and with  $x = 0.85$  after the EL treatment with an energy density of 260 mJ/cm<sup>2</sup> are presented. As it was mentioned, the narrow peak at 520 cm<sup>-1</sup>, which can be seen in spectra 1 and 2 is connected with scattering by the Si(001) substrate. As one can see, this peak in spectra 1 is slightly broadened in the region of low energy. This peculiarity can be well described by Lorentz curve BE1 (Table II, Fig. 2). It is reasonable to suppose that this peak is probably caused by scattering on optical phonons localized in SNs formed by the excimer laser treatment. In the Fig. 3 calculated (using a linear-chain model) frequencies of the phonon modes localized in silicon slabs versus its size, calculated data from our

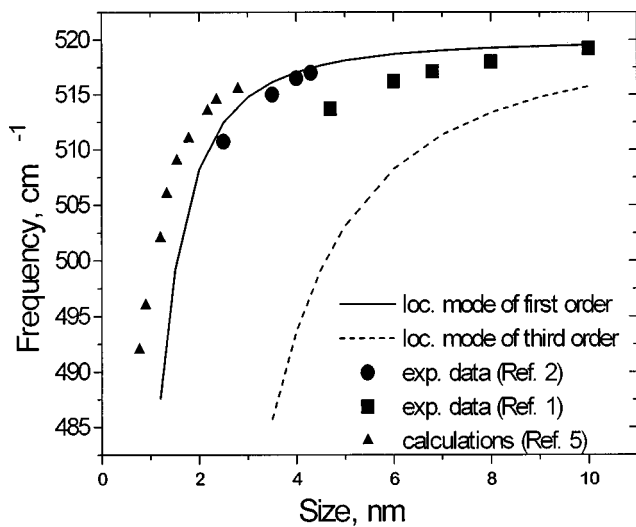


FIG. 3. Frequencies of localized optical phonon modes calculated in silicon slab model compared with experimental data from Refs. 1 and 2 and calculations from Ref. 5 for Si spheres using a bond polarizability model.

work,<sup>5</sup> and experimental data of other authors (concerning the Raman peak position versus the size of the Si nanocrystals) are presented. According to our evaluation (Fig. 3), being in good agreement with the direct experimental affirmation of other authors,<sup>2</sup> the size of the Si crystal nanoclusters should be about 2.5 nm. According to data from Zi *et al.*'s work,<sup>5</sup> where the Raman peak position was calculated using a bond polarizability model for Si spheres, the size of SNs should be even smaller. The small feature with position 465  $\text{cm}^{-1}$  is observed in spectrum 1, Fig. 2 (Lorentz curve BE2, Table II), and can be connected with additionally formed Si-Si local bonds during laser treatment.

In the case of the sample with a comparatively high concentration of excess silicon atoms ( $x=0.85$ ) dramatic changes in Raman scattering spectra are observed after the excimer laser treatment (spectra 2 in Fig. 2). According to our estimates (Fig. 3) peak CE1 (Table II) at 508  $\text{cm}^{-1}$  probably corresponds to scattering on phonons localized in SNs with an evaluated size of 2–2.5 nm. Peak CE2 at 493  $\text{cm}^{-1}$  (spectrum 2, Fig. 2, Table II) cannot be connected with scattering on a higher (third) mode because of the relationship between the phonon frequencies of the first and third localized modes (Fig. 3). Meanwhile, the second mode should be forbidden in Raman scattering. So, peak CE2 at 493  $\text{cm}^{-1}$  may be connected with silicon nanoclusters preexisting in  $\text{SiN}_x$  films ( $x=0.85$ ), with a size of about 1.3 nm. Due to the very short duration of the laser pulse (about 5 ns), diffusion of Si atoms should be neglected and a significant amount of excess silicon atoms remains in a dispersed state and determines the Raman signal from the Si-Si bond vibrations, corresponded to the CE3 peak at 473  $\text{cm}^{-1}$ .

After 2 h thermal annealing at 1200 °C strong changes in the Raman spectrum of sample with  $x=0.85$  have also occurred. One can observe in spectrum 2 in Fig. 4 a distinct asymmetry of the parasitic peak soaking from the substrate. This feature can be well approximated by the Lorentz curve with the position of 514  $\text{cm}^{-1}$  (peak CT1, Fig. 4, Table II). One can also clearly see peak CT2 at approximately 501  $\text{cm}^{-1}$ . From the experimental and theoretical data of various authors (see Fig. 3), one can suppose that if peak CT1 is

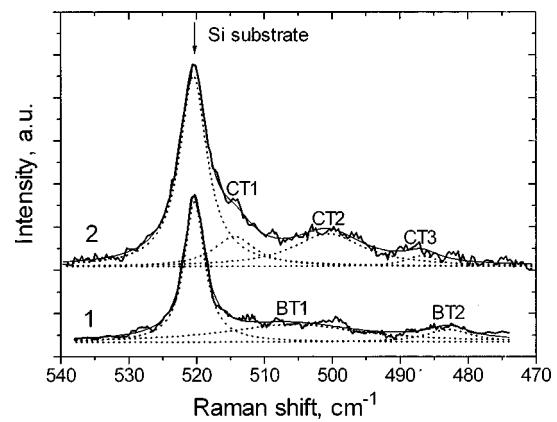


FIG. 4. Raman spectra of  $\text{SiN}_x$  films after thermal annealing at 1200 °C, 2h: 1,  $x=1.2$ , and 2,  $x=0.85$ .

related to scattering on the optic phonon modes of the first-order localized in silicon nanoclusters, then the size of these nanoclusters should be 3–5 nm. The position of peak CT2 (Fig. 4) well corresponds to scattering on the optical phonon modes of the third order localized in the nanoclusters (see the dashed line in Fig. 3). If it is right, one can affirm that the size dispersion of the obtained silicon nanoclusters in the  $\text{SiN}_x$  matrix is very small. But, it also can be supposed that the CT2 peak resulted by scattering on very small silicon clusters (about 1.5 nm), which were not gettered in bigger clusters in the process of annealing. In the sample with  $x=1.2$  there are small features in the Raman scattering spectrum: the BT1 region around 506  $\text{cm}^{-1}$  and peak BT2 with a position of 483  $\text{cm}^{-1}$ , but its intensities are very small and not more than the noise level, so one cannot clearly determine the presence of silicon nanoclusters in this sample. It should be mentioned that Raman intensities corresponded to disordered Si nanoclusters in as-deposited films (Si-Si bonds: peaks C1, C2; Si-N bonds: peak C3, Fig. 1) eliminated during thermal annealing (Fig. 4) in contrast to the laser treatment (Fig. 2), which may be explained as gathering of Si atoms in larger nanocrystals during thermal annealing due to diffusion.

Raman spectroscopy demonstrates strong changes in the phonon spectra of  $\text{SiN}_x$  films after thermal and laser annealing, that can be interpreted as the formation of crystalline silicon nanocrystals inside the films. Thermal annealing leads to gathering of Si atoms in nanocrystals with a size of about 3–5 nm. Using the nanosecond excimer laser treatment prevents diffusion of Si atoms and allows to us crystallize Si nanoclusters existing in as-deposited  $\text{SiN}_x$  films, which allows us to create nanocrystals with sizes from 1.5 up to 2.5 nm depending on the energy density of the laser irradiation and the value of the excess of silicon atoms.

<sup>1</sup>Z. Iqbal, S. Veprek, A. P. Webb, and P. Capezzuto, *Solid State Commun.* **37**, 993 (1981).

<sup>2</sup>G.-X. Cheng, H. Xia, K.-J. Chen, W. Zhang, and X.-K. Zhang, *Phys. Status Solidi A* **118**, K51 (1990).

<sup>3</sup>H. Kakinuma, M. Mohri, M. Sacamoto, and T. Tsuruoka, *J. Appl. Phys.* **70**, 7374 (1991).

<sup>4</sup>G. Yu, G. Chen, and F. Zhang, *Phys. Status Solidi B* **152**, 73 (1989).

<sup>5</sup>J. Zi, H. Büscher, C. Falter, W. Ludwig, K. Zhang, and X. Xie, *Appl. Phys. Lett.* **69**, 200 (1996).