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Silicon nanocrystals by thermal annealing of Si-rich silicon oxide prepared by the LPCVD method

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Abstract

The Si-rich silicon oxide (SiO_x) thin films are prepared on silicon crystalline substrates by low pressure chemical vapor deposition (LPCVD) method. The oxygen concentration x are controlled by the ratio of the partial pressures of N_2O and SiH_4 gases in the reaction chamber. In order to induce the phase separation on SiO_2 and Si nanostructures the samples are annealed at the temperatures 900–1100 °C. The structural and optical properties of the samples are investigated by Raman and infrared spectroscopy and scanning electron microscopy.
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Keywords: Si-rich silicon oxide; LPCVD; Raman scattering; Low frequency particle modes

1. Introduction

The growth of thin films by low pressure chemical vapor deposition (LPCVD) is one of the most important techniques for deposition of thin films in modern technology. The reasons of a broad application of the LPCVD method are in possibility of deposition of different elements and compounds at relatively low temperatures in amorphous and crystalline phase with high degree of uniformity and purity. A simple handling, high reliability of operations, fast deposition, homogeneity of deposited layers and high reproducibility are the basic characteristics the LPCVD method.

Apart from vitreous silica as the archetypal oxide network former and the basis of traditional silicate glasses other amorphous oxides of silicon such as silicon monoxide and silicon sesquioxide (Si_2O_3) also exists. These amorphous silicon suboxides have been known for decades and are used in a variety of technical applications. The possibility of phase separation of silicon suboxides into silicon and SiO_2 was first proposed by Brady [1]. On the basis of a theoretical approach this concept was discussed in more detail by Temkin [2] who proposed a random-mixture (RM) model. The RM model assumes small domains in which either silicon is bonded only to silicon or to oxygen. This corresponds to a two-phase mixture of Si and SiO_2 domains with thin boundary layer of ≈10 Å between [2]. Dupree et al. [3] performed magic-angle spinning (MAS) NMR investigations on silicon monoxide and estimated phase separated regions of Si and SiO_2 near to 20 Å.

In this paper we show the results of the LPCVD deposition of non stoichiometric oxide SiO_x thin films with SiH_4 and N_2O precursors. The chemical reaction we used is oxi-

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dation of silane with N_2O: $SiH_4 + \gamma N_2O \rightarrow p\text{-}SiO_x + (1-p)SiH_4 + 2pH_2 + (\gamma - px)N_2O + px\ N_2$. The silicon nanocrystals were formed by phase separation of SiO_x ($x < 2$) structure induced by thermal annealing: $SiO_x \rightarrow (1 - x/2)\,Si + x/2\,SiO_2$, where N_2O/SiH_4 ratio controls the Si amount in the layer.

2. Experimental

The LPCVD method is most successfully applied in deposition of polysilicon thin films from SiH_4 in the temperature range 580–660 °C and SiO_2 layers from SiH_2Cl_2 at 900 °C. The scheme of the conventional hot-wall horizontal LPCVD reactor is shown in Fig. 1. The base of device is a quartz tube placed in a spiral heater. The tube is evacuated on the pressure of 0.1 Pa and heated on to the wanted temperature to 1000 °C. The temperature stability is ±1 °C. The deposition starts with entering of the working gas in the tube. The working (dynamical) pressure is 10–200 Pa.

In this experiment the non-stoichiometric oxide SiO_x ($x < 2$) were deposited on 0.65 μm thick thermal oxide on a (111) oriented silicon substrate with a diameter of 50 mm set at 7 mm from the 1st (dummy) wafer. The depositions were carried out by thermal decomposition of 2% (S1) and 26% silane (S2 and S3) diluted in argon. The deposition temperatures was 748 °C. The flow rate ratios of nitrous oxide and silane $\Phi(N_2O)/\Phi(SiH_4)$ are presented in Table 1. The SiO_x films were further thermally annealed at 900, 1000 and 1100 °C in air. Upon annealing the decomposition of SiO_x into SiO_2 and elemental Si takes place. After the decomposition, the excess Si atoms form Si clusters embedded in a SiO_2 matrix. The size of Si clusters is expected to become larger for the higher annealing temperatures. The deposited layers were characterized by Raman spectroscopy using Dilor Z-24 Raman triple monochromator spectrometer, IR absorption spectroscopy and scanning electron microscopy (SEM).

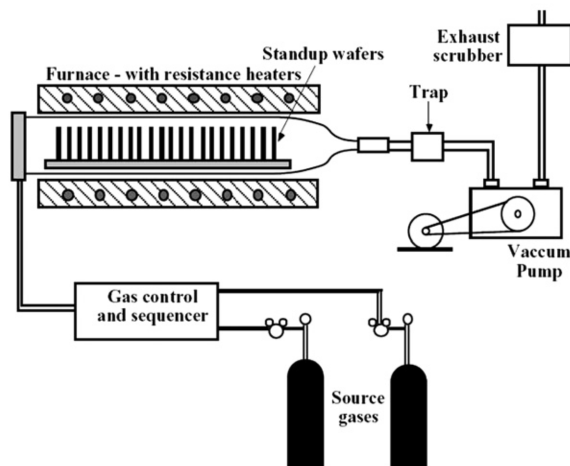

Fig. 1. Schematic description of the LPCVD device.

Table 1
Deposition parameters of SiO_x thin films

Sample	$\Phi(SiH_4)$/sccm	$\Phi(N_2O)/\Phi(SiH_4)$
S1	6.2	4.04
S2	37.7	1.14
S3	80.5	1.03

3. Results and discussion

The main difference between CVD depositions at low pressure and atmospheric pressure is in ratio of the mass transport velocity and the velocity of reaction on the surface. At atmospheric pressure these quantities are of the same order of magnitude. While the velocity of the mass transport depends mainly on the reactant concentration, diffusion, and thickness of the border layer, the velocity of the surface reaction depends mainly on the concentration of reactants and temperature. As diffusion of gas is reciprocal to pressure, it will decrease 1000 times if the pressure reduces from atmospheric value to 100 Pa. Now the carrier gas is not more necessary, the substrates could approach more closely, and deposited films shows better uniformity and homogeneity. The working gas, that regularly consist of the gas for dilution and of the reactive gas, after entering spreads inside the tube and flows above the hot substrates (thin wafers of silicon, quartz or some other material) placed in the quartz holders. The wafers in the tube reactor are radiantly heated by resistive hearing coils surrounding the tube. The critical factors that influence on thickness uniformity and film content are positions of the substrates, temperature profile in the zone of deposition, reactor geometry, deposition time, working pressure, as well as the quantity and content of all gases or vapors that enter in the reactor.

Fig. 2a shows the FTIR spectrum of the sample S1. The band above 1000 cm^{-1} is assigned to the asymmetric stretching of the Si–O–Si bridge. This peak position can be used for reasonable stoichiometry estimation in case of a homogeneous SiO_x alloy [4]. The observed peak position at 1072 cm^{-1}, which differs from the position of thermally grown oxide at ~1080 cm^{-1}, gives the composition $x = 1.9$. The SEM image in Fig. 2b shows that the layer is porous and in homogeneous. These results show that the structure of deposited layer is more close to the silica structure than to SiO structure.

In order to decrease the composition x we have decreased the flow rate ratio to: $\Phi(N_2O)/\Phi(SiH_4) = 1.14$ (sample S2). Fig. 3 shows the Raman spectra of as deposited and annealed samples. The Raman spectra shows the characteristic bands of SiO_x structure that consists of the broad peaks at 160 and 460 cm^{-1} which corresponds to the TO and TA phonon-like bands. Upon thermal annealing the decomposition of SiO_x into SiO_2 and elemental Si

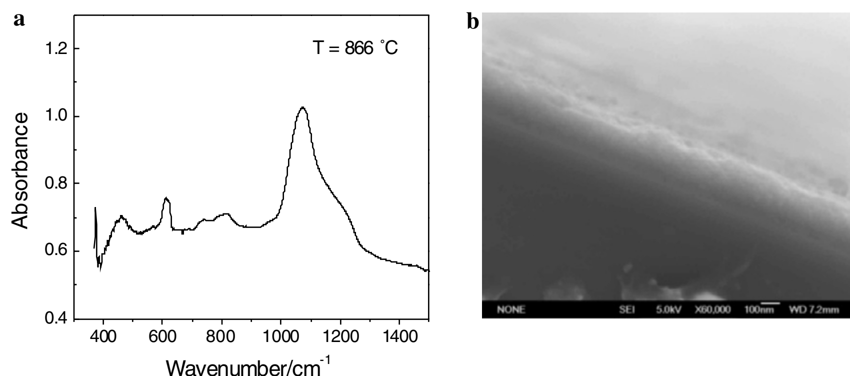

Fig. 2. FTIR spectrum (a) and SEM image (b) of the sample S1.

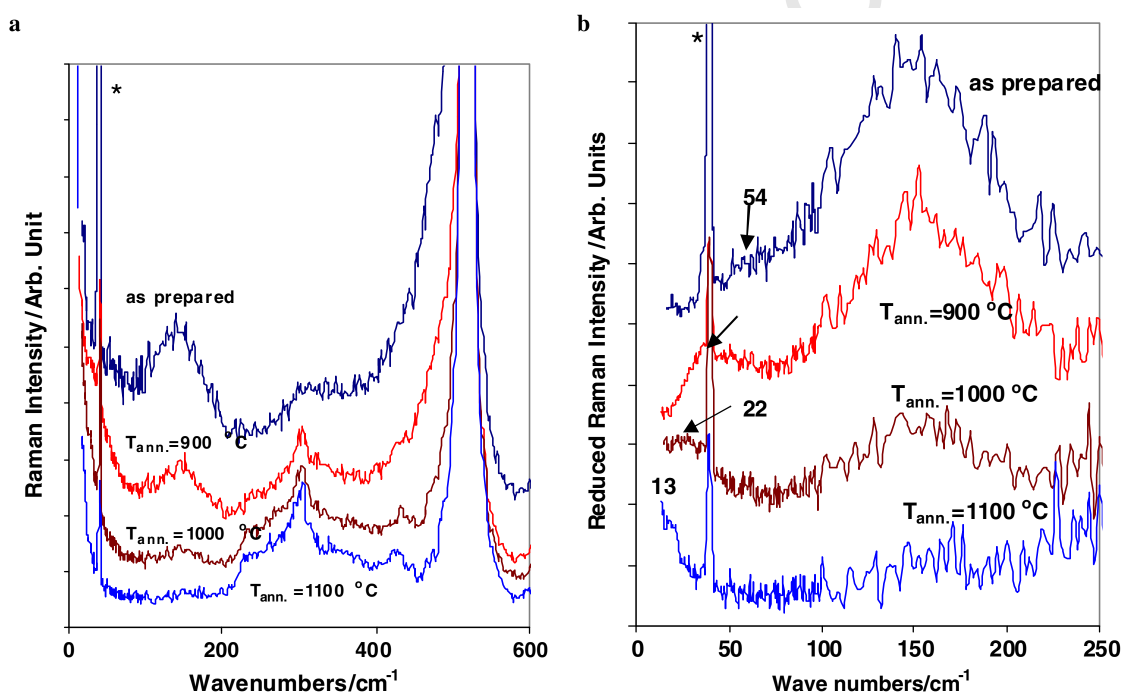

Fig. 3. Raman spectra of SiO_x structure in the range of TA and TO phonon-like bands of the sample deposited at 748°C with the gas flow rate ratio $\Phi(N_2O)/\Phi\ (SiH_4) = 1.14$ (a); the low frequency reduced Raman spectra of the same samples (b) the arrow indicate the symmetric vibrational mode of silicon nanoparticles. The asterisk indicates the plasma line at 39 cm^{-1}.

takes place. After decomposition, the excess Si atoms form Si clusters embedded in a SiO_2 matrix. The size of Si clusters is expected to become larger for higher annealing temperatures. The Raman scattering on nanosized silicon particle manifests in broadening and red shift of the TO(γ) phonon band at 521 cm^{-1} and blue shift of the low frequency spherical mode with decrease of particle size. The model of phonon confinement of optical modes [5] and the calculation of spherical acoustical modes are applied in order to deduce the mean size and distribution width of silicon nanocrystals [6].

Low frequency modes indicated by an arrow in Fig. 3b corresponds to the spherical acoustical modes of silicon nanocrystals. Vibrations of elastic spheres have been studied for a long time by Lamb [7]. The frequency (in wavenumbers) of the symmetric spherical mode is given by [8]:

$$v_0 = \frac{S_0 v_L}{cD}, \quad (1)$$

where v_0 is the frequency of the surface symmetric modes, D is the diameter of the spherical particle and c is the velocity of light. The constant $S_0 = 0.76$ [6]. The mean value of the longitudinal sound velocities calculated across three crystalline directions is $v_L = 8790$ m/s. These parameters when inserted in Eq. (1) give the mean size of silicon nanoparticles from the know frequency of the symmetric spherical mode, i.e. $D = 2.29 \times 1^{-7}/v_o$. Experimentally, by comparison of the low frequency Raman results with the particles size distributions obtained by TEM, the size of silicon particles deduced by Eq. (1) are by the factor of 0.5 smaller [6]. The reason for such factor is still unclear and could be connected with the resonance phenomena of inci-

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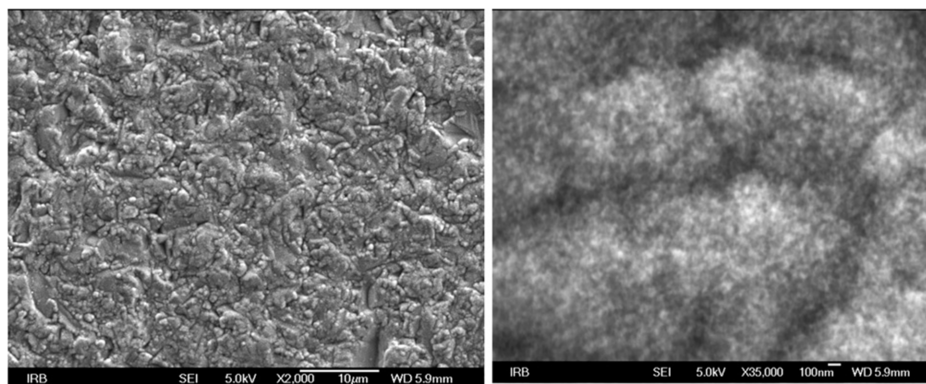

Fig. 4. SEM images of the SiO_x film prepared at 748 °C by silane reaction with N_2O at flow rate: $\Phi(SiH_4) = 80.5$ sccm, and gas flow rate ratio: $\Phi(N_2O)/\Phi(SiH_4) = 1.03$.

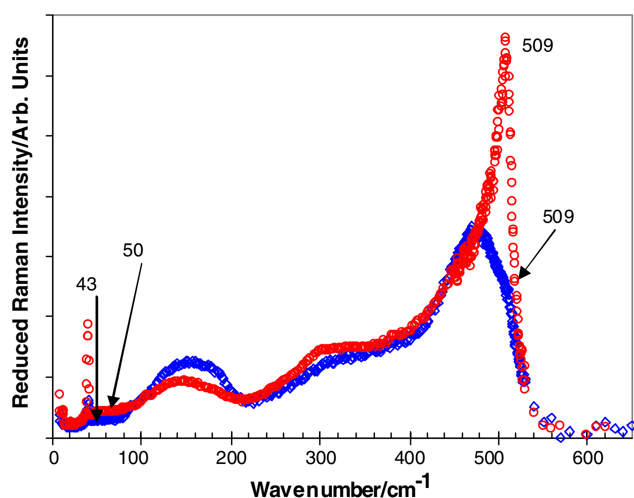

Fig. 5. Raman spectra reduced for the Bose–Einstein factor of SiO_x prepared with silane flow rate $\Phi(SiH_4) = 80.5$ sccm, and gas flow rate ratio: $\Phi(N_2O)/\Phi(SiH_4) = 1.03$ (circles) and of the same sample annealed at 900 °C for 1 h in air (diamonds). The asterisk indicates the plasma line at 39 cm^{-1}.

168 dent laser energy with the exciton transition in silicon [6].
169 Taking this into the consideration, the silicon nanocrystals
170 with mean sizes of 3.2, 5.2 and 8.8 nm are formed in the
171 films annealed at 900, 1000 and 1100 °C, respectively. Some
172 broad bands with maximum at 54 cm^{-1} also exist for the as
173 deposited samples. This could be also ascribed to spherical
174 vibrations that correspond to the broad distribution of sil-
175 icon nanoparticles. The mean particles size of 2.2 nm esti-
176 mated from the peak maximum agree with the value
177 obtained by NMR measurements of Dupree et al. [3].
178 With further decrease of the flow rate ratio to $\Phi(N_2O)/$
179 $\Phi(SiH_4) = 1.03$ (sample S3), the black porous structure
180 with porous surface morphology shown in Fig. 4 is
181 obtained. The sample is than further annealed at 900 °C
182 for 1 h in air. The low frequency Raman spectra of the as
183 deposited and annealed sample shows the broad peaks of
184 spherical modes peak with maximums at 43 and 50 cm^{-1}
185 which corresponds to the mean particle size of 2.7 and
186 2.3 nm, respectively. The existence of such small crystallites
187 are also confirmed by the Raman scattering on the confined
188 TO(Γ) phonon mode that appear as a shoulder and sharp
189 peak at 509 cm^{-1} of the as prepared and annealed sample.
190 By applying the phonon confinement model, the mean par-
191 ticle size is possible to obtain by the relation [5]: $D = 0.337/$
192 $(521/v\text{-}1)$, where v is observed frequency of TO(Γ) phonon
193 mode. The particles of mean size of 1.4 nm were found by
194 this formula which is similar to those found from the LFR
195 modes Fig. 5.
196 As a conclusion here we have shown that by using
197 LPCVD technique a number of different silicon SiO_x nano-
198 structures important for microelectronic and photonic
199 application is possible to prepare with rather simple
200 approach. The content of oxygen atoms is possible to con-
201 trol by of nitrous oxide and silane partial pressure gas ratio
202 and the particle size by the temperature of annealing pro-
203 cess. The different size of silicon nanocrystals in silica
204 matrix are obtained by subsequent annealing of SiO_x struc-
205 ture. The Raman scattering techniques showed to be simple
206 and reliable technique in determination of size of prepared
207 silicon nanoparticles.

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