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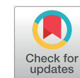
Effect of annealing in oxidizing atmosphere on optical and structural properties of silicon suboxide thin films obtained by gas-jet electron beam plasma chemical vapor deposition method



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ABSTRACT

The effect of the annealing temperature on the optical and structural properties of the a-SiO_x:H thin films prepared by gas-jet electron beam plasma chemical vapor deposition method was studied. Annealing was carried out at 600, 700, 800, 900 and 1000 °C for 4 h in oxidizing atmosphere. According to FTIR spectroscopy measurements, the oxygen and hydrogen concentration in the as-deposited films was 25 at.% and 2 at.%, respectively. The SEM image showed that the as-deposited material had column structure with a large number of vertical voids. As a result of annealing, the thickness of the films decreased by approximately 1.5 times for all samples. The value of refractive index at 650 nm decreased from 2.5 to 2.0 with the increase of the annealing temperature. The E_{04} optical gap decreased in comparison with the value of the as-deposited thin films for 600 °C and 700 °C, and increased for 800 −1000 °C. For annealing at a temperature of 600 °C, the structure of the material changes insignificantly. A rearrangement in the structure of the matrix with the formation of amorphous silicon nanoclusters occurs at 700 °C and 800 °C. Annealing at the higher temperatures leads to transition from a material with amorphous nanoclusters to a material with nanocrystallites.

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1. Introduction

Thin films consisting of silicon nanocrystallites in a silicon suboxide matrix (nc-Si/SiO_x) attract close attention, both in connection with the study of their properties associated with quantum-size effects, and with the prospects of practical applications [1,2]. In particular, nc-Si/SiO_x thin films are attractive due to compatibility with the microelectronics industry, exhibit chemical stability, optical transparency [3], room temperature photoluminescence in the visible region of the spectrum [4,5] and could be promising candidates as building blocks in photovoltaic [6], optoelectronic, and nanoelectronic devices [7,8]. Moreover, a nc-Si/SiO_x structure has high relevance as a basic element in SiO_x/SiO_2 superlattices [9,10].

The two-step method is widely used for the synthesis of such structures. During the first stage, a non-stoichiometric silicon oxide film is being synthesized. At the second stage, high-temperature annealing of the initial material leads to solid-phase crystallization process [11] with the formation of silicon nanoclusters or/and nanocrystallites in the silicon oxide matrix. The properties of the material after annealing (degree of crystallinity, crystallite size, photoluminescence, etc.) are strongly dependent on the synthesis method of as-deposited films [12].

Generally for subsequent thermal annealing, silicon suboxide films are synthesized by electron cyclotron resonance chemical vapor deposition (ECRCVD) [13], plasma-enhanced CVD (PECVD) [14], inductively coupled plasma enhanced chemical vapor deposition (ICPECVD) [15], hot filament chemical vapor deposition (HFCVD) [16] and low pressure chemical vapor deposition (LPCVD) [17]. In this work, silicon suboxide films were obtained by the gas-jet electron beam plasma chemical vapor deposition (GJ EBP CVD) method. Previously, this method was already used for deposition of

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silicon suboxide films [18], but they weren't subjected to thermal annealing. Besides the initial morphology of films, the annealing temperature strongly affects their structure and optical properties [19]. At temperatures up to 800 °C, the process of the formation of amorphous silicon nanoclusters in the silicon suboxide matrix takes place. The process of solid-phase crystallization with formation of silicon crystallites occurs at a temperature of more than 900 °C. Therefore, in this work the annealing temperature in the range 600–1000°C was chosen.

In this work, annealing was carried out in the oxidizing atmosphere (Ar and O_2 mixture). A number of studies examined the possibility of the increase of the photoluminescence of nanocomposite silicon films by thermal annealing in an oxygen-containing atmosphere [20–22]. Such thermal annealing leads to good passivation of silicon dangling bonds on the surface of silicon nanoclusters with oxygen atoms and the elimination of hydrogen active impurities [21]. But oxidation can lead to a decrease in the size of nanoclusters accordingly changing the photoluminescence spectrum [23]. The processes of formation (phase separation) and oxidation of silicon nanoclusters occur simultaneously during annealing and are in fact competing processes.

The objective of this work was to study the effect of the annealing temperature in the range 600–1000°C on the structure and optical properties of the amorphous hydrogenated silicon suboxide (a-SiO_x:H) thin films prepared by gas-jet electron beam plasma chemical vapor deposition method.

2. Experimental details

In this work, a-SiO_x:H thin films were obtained by the GJ EBP CVD method. This method is based on the expansion of a gas into a vacuum with the formation of a supersonic jet, which is then activated by electron-beam plasma. As a result of the interaction of electrons with gas molecules, they dissociate and activate with the formation of ions and radicals. The gas jet transfers the formed ions and radicals to the substrate on which the thin film grows. Previously, this method was also used to obtain silicon oxide nanowires [24].

The synthesis was carried out from a mixture of gases H_2, O_2, and 5%SiH_4+95%Ar with the flow rates 386, 3 and 89 sccm, respectively. It should be noted that hydrogen and a mixture of monosilane and argon were supplied into the chamber through a 2 mm nozzle, while oxygen was supplied through a leak valve. During the synthesis, the substrate temperature, the vacuum chamber pressure, the electron beam energy, and current were 260 °C, 18 Pa, 600 eV and 80 mA, respectively. To obtain films with a thickness of approximately 500 nm, the synthesis time was 30 min. The a-SiO_x:H films were deposited on one monocrystalline silicon (c-Si) wafer for SEM and Fourier transform infrared (FTIR) spectroscopy measurements and on five quartz substrates for Raman, x-ray diffraction and optical measurements.

After the deposition of the films, the samples obtained on quartz and c-Si substrates were removed from the vacuum chamber and placed in a quartz tube oven. In order to form silicon clusters in silicon oxide matrix, the films on quartz substrates were thermally annealed at 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C for 4 h in oxidizing atmosphere (Ar and O_2 mixture at the ratio of 1000:1) and the film on c-Si wafer was thermally annealed at 800 °C under the same conditions. The heating rate was kept constant – 5 °C/min. The names of the samples, the substrate material, and the annealing temperature are given in Table 1.

The composition (bonded oxygen and hydrogen concentration) and bond structure of as-deposited film obtained on c-Si wafer were investigated by FTIR spectrometry. FTIR spectra were recorded with Bruker IFS-113 V Fourier spectrometer in the wavenumber range of 400–4000 cm^{-1} with a 1 cm^{-1} resolution. The procedure used for obtaining of the concentration of bonded oxygen and hydrogen in the thin film is described in Ref. [18].

Table 1
Substrate material and annealing temperature of the samples.

Sample	Substrate material	Annealing temperature, °C
AN1	quartz	600
AN2	quartz	700
AN3	quartz	800
AN4	quartz	900
AN5	quartz	1000
AN6	c-Si	800

The morphology and thickness of the as-deposited thin film obtained on c-Si wafer were determined by the scanning electron microscopy (SEM) method using the JEOL JSM-6700 F microscope. The SEM was equipped with an X-ray energy dispersive spectroscopy (EDS) unit that was used to estimate the elemental composition of the as-deposited and annealed films on quartz substrates.

The films crystallinity, as well as the size of the crystallites was determined by Raman spectroscopy on the spectrometer Horiba Jobin Yvon T64000 using the 514 nm line of an Ar^+ laser as the exciting source. The procedure used for obtaining of the crystallite size and the degree of crystallinity is described in Ref. [25].

Also the size of the crystallites were evaluated by x-ray diffraction (XRD) spectroscopy. XRD patterns were recorded using time resolved diffractometry station (channel 5 b, VEPP-3) of the Siberian Synchrotron and Terahertz Radiation Center (X-ray detector OD-3M, wavelength - 1.516 Å) [26].

The optical transmittance spectra of the samples obtained on quartz substrates were measured by DFS-452s spectrometer equipped with a photodiode array and a tungsten lamp as a source of radiation. The transmission spectra of the as-deposited and annealed films were used to determine their thicknesses, refractive indices and E_{04} optical gaps. E_{04} optical gap was defined as the photon energy corresponding to an absorption coefficient of 10^4 cm^{-1}. This value acts as a measure for the optical band gap energy. The thicknesses and optical parameters of thin films were determined using PUMA code which is widely used for characterization of amorphous [27] and nanocrystalline [28] silicon-containing films.

Photoluminescence (PL) of annealed films was obtained using a helium-cadmium laser with a wavelength of 325 nm and a power of 10 mW as an excitation source at a room temperature.

3. Results and discussion

3.1. As-deposited films

In addition to the values of the films thicknesses extracted from optical transmittance, the thickness of the film deposited on c-Si wafer was obtained from a cross-section SEM image of the as-deposited sample AN6 (Fig. 1). The value of the thickness obtained from SEM is about 521 nm and is in a good agreement with the thicknesses extracted from the transmittance that lie in the range of 520 ± 50 nm. Also, the SEM image shows that the a-SiO_x:H thin film has a column structure with a large number of vertical voids.

Since the FTIR is one of the most utilized techniques providing quantitative information about bonded oxygen and hydrogen content in silicon suboxide films, but not applicable in the case of using quartz as substrate, such measurements for as-deposited film were made on the c-Si wafer. We assume that the values of the concentration are identical for films synthesized on c-Si wafer and

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