SILICON-BASED NANOSTRUCTURED MATERIALS

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Abstract: The paper presents different classes of silicon-based nanostructured materials. Their microstructure is investigated by means of conventional and high-resolution transmission electron microscopy. Both equilibrium and non-equilibrium electrical properties are studied, in a temperature range that goes from liquid nitrogen to room temperature. Some optical properties are also considered. Quantum confinement effects are evidenced and modeled.

Key words: Silicon nanocrystals, electron microscopy, electrical properties, optical properties, and quantum confinement.

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1. INTRODUCTION

The great interest aroused by the nanocrystalline silicon films has originated in the discovery of the bright photoluminescence (PL) at room temperature (RT) of the porous silicon (PS) [1, 2], as well as of silicon nanodots embedded in silicon dioxide (see [3]). This fact suggested the possibility of using nanocrystalline silicon (nc-Si) in optoelectronics [4-7], that would be very convenient as the silicon is the most used material in micro- and nano-electronics. For optoelectronic devices, multiquantum wells and superlattices with nc-Si layers are used. The specific properties of nc-Si also lead to other possible applications, such as gas sensors [8-10], or capacitors [11].

Electron microscopy studies of nc-Si films have shown various microstructure aspects, depending on the preparation conditions [5, 12, 13]. High-resolution imaging exhibits complex fractal geometry for PS and multi-twinning of the nanodots.

The electrical transport properties of nc-Si are determined mainly by its microstructure. Various transport mechanisms were investigated to explain the different experimental results, and several models were proposed: hopping at low temperatures and thermal activation at high temperatures [14], Poole-Frenkel mechanism [15], fractal percolation [16], generation-recombination phenomena in the depletion region [17], dangling bonds [18], thermally assisted tunneling [19-21], and tunneling under Coulomb blockade [22].

In this paper several aspects concerning the microstructure, electrical behavior and photoluminescence of nc-Si are discussed. Section 2 deals with preparation of PS layers and Si/SiO₂ nanocomposite films. Their microstructure is analyzed in Section 3. In Section 4, experimental measurements of the conduction properties, together with a theoretical model, are presented. The photoluminescence of these films is studied in Section 5. In the last Section, concluding remarks are presented.
2. PREPARATION

The nanocrystalline PS layers were obtained by electrochemical etching [23-25]. P-type (100) Si wafers (5-15 Ωcm resistivity) were etched using HF (49%)-C₂H₅OH (1:1 volume ratio), under constant 5 – 15 mA/cm² current density. After the etching, the samples were illuminated for 1.5 – 3 min in situ with a Xenon lamp, in order to activate the photoluminescence. Some of the samples were oxidized. Al electrodes in sandwich configuration were thermally deposited.

The Si/SiO₂ nanocomposite films were prepared by co-sputtering. Two semicircle targets of 13.2 cm diameter and containing Si and SiO₂ respectively were used. The quartz slide substrate was located 5 cm above the targets. The sputtering took place for 12 hours under a residual pressure of 5x10⁻⁷ Torr, in a pure (99.9995%) Argon atmosphere of 19 mTorr. A RF voltage between substrate and target of 110 V, and a forward power of 180 W were applied. Under these conditions, films with variable Si concentration in SiO₂ (from x = 0 vol. % to x = 100 vol. %) are obtained at a single deposition. Their thickness is about 9 μm and the center of the slide corresponds to x = 45 vol. % of silicon. 50 parallel Al electrodes were deposited in a coplanar configuration.

3. MICROSTRUCTURE

To study the microstructure of nc-Si (PS and Si/SiO₂ nanocomposites), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with selected area electron diffraction (SAED) methods were used [25, 26]. These investigations were performed with a TEMSCAN JEOL 200CX analytic electron microscope and a high resolution TOPCON 002B microscope.

The investigated PS films have thicknesses of 10 and 15 μm. The ion milling was made by a Gatan instrument with two argon ion guns at 3.5 kV. The TEM cross-sectional specimens were prepared with M-bond glue. In order to have the fluid glue penetrating the pores, it was heated only after 24 h. The TEM specimens of Si/SiO₂ nanocomposites were prepared by scratching the sample layer with a diamond knife and collecting the small fragments on a carbon grid.

Fig. 1 ([25]) presents SEM cross-sectional images of PS film fractured near the (100) and the (110) Si planes. One can observe an alveolar columnar structure, with non-regular pores of 1.5 – 3 μm diameter (hereafter called macropores), that go through the whole PS layer thickness. The walls separating them have 100 – 200 nm thicknesses. Therefore, the estimated macroporosity of films is about 80%.

The alveolar walls were investigated by TEM. The TEM image of the [110] orientation projection of the alveolar wall is presented in Fig. 2a [25]. Fig. 2b shows a high resolution detail and Fig. 2c the corresponding SAED pattern. One can see that the crystalline structure is perfectly conserved. The fringes spacing of 0.314 nm corresponds to the {111} lattice plane spacing for Si crystals (0.3135 nm). This {111} plane spacing allows us to estimate the nanocrystallite sizes (1 – 3 nm). The nanoporosity of the alveolar walls is less than 50 %. The walls are structured in a nanowire network and thus the PS films present a double scale porosity.
Fig. 1. - SEM images of the cross sections of PS film (fractured silicon wafer): (a) image of cross section nearly parallel with (100) plane of silicon (perpendicular to PS film) and (b) image of an oblique cross section nearly parallel to the (110) cleavage plane of silicon [25].

Fig. 2. - Nanostructure of the alveolar wall viewed in (a) [110] orientation and (b) high-resolution detail with (c) the corresponding SAED pattern [25].

Fig. 3 shows the high resolution TEM image of the Si/SiO$_2$ nanocomposite in the region with x = 50 vol. %. One can observe a rather non-uniform distribution of Si nanocrystallites in an amorphous SiO$_2$ matrix and also the presence of nanotwins inside the Si nanocrystallites. It is important to remark that while the silicon crystallites increase in size with the silicon concentration, they remain isolated.
Fig. 3. - HRTEM image showing the presence of the nanotwinning in the silicon nanocrystallites.

4. ELECTRICAL TRANSPORT

The current–voltage (I – V) characteristics at room temperature (RT) and the current–temperature (I – T) ones were taken using a Keithley 642 electrometer, a Keithley 2000 multimeter and an Agilent E3631A d.c. power supply.

Fresh PS samples have a slow rectifying behavior in the whole voltage range [24]. On the contrary, the oxidized samples have a strong rectifying behavior (Fig. 4a [24]). Up to 2.2 V in forward bias the curve is exponential, and then it becomes practically linear, due to the very high series resistance of the PS film. At the same time, in this quasi-linear region, one can observe a number of percolation thresholds. The I – T curves for PS were measured in the 150 – 300 K range, at low voltages (1 – 2 V), for both fresh and oxidized samples. Fresh samples have one activation energy (0.49 – 0.55 eV) on the whole temperature range [24], while the oxidized ones present two activation energies (Fig. 4b, [24]). At low temperatures the activation energy is 0.50 – 0.60 eV, while over about 280 K, a new activation energy of 1.20 – 1.80 eV appears.

I – V characteristics for Si/SiO₂ samples are shown in Fig. 5. The three curves correspond to the Si concentrations of 68, 70 and 73 vol. %. The curves are practically symmetric and superlinear. From the microstructure investigations it results that the carrier transport takes place mainly by tunneling under Coulomb blockade [27-29]. The corresponding relations are in excellent agreement with the experimental data. The I – T dependence was measured between the liquid nitrogen temperature and RT on the 73 vol. % Si concentration sample, for biases of 1, 4, 5, and 25 V. For all the biases, two values for the activation energy, \( E_1 = 0.30 \text{ eV} \) and \( E_2 = 0.51 \text{ eV} \), were found.
Fig. 4. (a) I – V characteristic for oxidized PS samples at RT [24]; (b) I – T characteristic for oxidized PS samples: □ U₂ = 2 V (‘+’ on c-Si), □ U₃ = -2 V [24].

Fig. 5. - I – V characteristics for Si/SiO₂ at RT.

To explain the conduction properties of the nc-Si films we have proposed a quantum confinement model [24, 25, 30, 31]. In the case of the PS films, the ratio between the nanowire length and diameter is about 10³ – 10⁴. Therefore, the electron Hamiltonian can be split in a 1D longitudinal part (along the wire) and a 2D transversal one. The longitudinal part corresponds to a 1D crystal with a direct band gap. The transversal part is modeled by a 2D infinite quantum well. Both circular and square symmetry of the quantum well were considered. Then, the electron energy is

\[
E = \left( \varepsilon_{n,k_z} + \frac{2\pi^2\hbar^2}{m^*a^2} k_z^2 \right) + \frac{2\pi^2\hbar^2}{m^*d^2} \left( \frac{1}{k_{z,p+1}^2} - \frac{1}{k_{z,0,1}^2} \right) \equiv \varepsilon_{n,k_z} + E_{k_z},
\]  

(1)
where $\varepsilon_{n,k,1}^l$ is the shifted energy of the longitudinal motion, $E_{l,p}$ are the discrete levels of the transversal motion (by definition, $E_{0,0}(=0)$, $m^*$ is the transversal effective mass, $d$ is the wire diameter (for square well, $d$ is the square diagonal) and $z_{l,p} = \pi x_{l,p}$ represents the $p$-th zero of the Bessel function $J_0(z)$ for circular symmetry or $x_{l,p} = \sqrt{l^2 + p^2}$ for square symmetry (with $2p = n_x + n_y$ and $2l = |n_x - n_y|$, $n_x$ and $n_y$ being the infinite square quantum well numbers).

In both cases, $l$ represents the orbital quantum number.

Thus, the quantum confinement introduces discrete levels into the enlarged band gap of the 1D wires, so that $E_{l,p}$ can be identified with the activation energies measured in the I – T characteristics. The ratio of the first two activation energies is $E_{0,2}/E_{0,1}$ (since a longitudinal electric field cannot produce an orbital motion) and has the value 2.799 for circular symmetry and 2.667 for square one, while the average experimental value is 2.727. For the real finite quantum well (of 2.2 eV, see the I – V characteristics), this ratio is modified with about 0.7 % for both symmetries. From Eq. (1), with $m^* \equiv 0.669m_0$, one also obtains for an average activation energy of 0.55 eV a diameter of 3.2 nm for circular symmetry and 3.5 nm for square one.

During the heating, the electrons will be excited from the valence band to the second energy level only after the first one will be fully occupied. The degeneracy of the levels is proportional to $d^2$, so it is reduced by oxidation. Therefore, the diameter decrease will produce a decrease of the temperature at which the first level is fully occupied and then a second activation energy will appear.

A similar model can be used to describe the behavior of the nanodots network in Si/SiO$_2$. For spherical symmetry, the energy levels $E_{l,p}$ will have the same expression, with $z_{l,p}$ the $p$-th zeros of the spherical Bessel functions $j_l(z)$. The Coulombian repulsion forbids the presence of more than one non-compensated carrier in a nanodot. Then, the activation energy of the dark current is given by the difference between the consecutive energy levels. If the applied electric field is strong enough, it will imply the additional condition of the angular momentum conservation. The ratio of the observed activation energies is $E_{2}/E_{1} = 1.70$, corresponding to $E_1 = \varepsilon_{0,1} - \varepsilon_{0,0}$ and $E_2 = \varepsilon_{0,2} - \varepsilon_{0,1}$, with a mean nanodot diameter of 3.9 nm.

5. PHOTOLUMINESCENCE

In nc-Si, the bright PL in the visible range (unusual for bulk Si) is due to both quantum confinement and surface/interface effects. The PL of PS was measured at RT. The samples were excited with monochromatic light ($\lambda = 352$ nm, $P = 1$ W) from a krypton laser. The chopping frequency was 433 Hz. The detection was made with a GaAs photomultiplier (~30 °C, ~1500 V). Fig. 6 [32] presents four PL spectra. Curves 2 – 4 correspond to different anodization ($t_a$) and illumination ($t_{ill}$) times during the samples preparation. For the first time the broad PL band (1.4 – 2.2 eV) was split under experimental conditions in two subbands with maxima situated at 1.54 eV (curves 3, 4, $t_{ill} = 2$ min) and 1.72 eV (curve 2, $t_{ill} = 3$ min). While the illumination time modifies the peak position, the anodization time determines the intensity (the film thickness: $t_{a} = 90$ min, $t_{a}=30$ min). The enveloping curve 1, taken on the sample 2, after 16 weeks of storage in air, contains both subbands of the visible PL.
Similar PL results with those on PS were obtained on Si/SiO$_2$ at small Si concentration (under the electrical percolation threshold). The maximum position shifts towards higher energy with the decrease of the nanodot diameter, i.e. of the Si concentration. No PL was observed on samples with significant electrical transport, due to the interface non-radiative recombination.

6. CONCLUSIONS

The PS microstructural investigations show a two-levels porosity: a system of columnar macropores that cross the whole film thickness and a nanopore structure of the alveolar walls that forms a nanowire network. Si/SiO$_2$ nanocomposites are formed by Si (multi)twinned nanocrystals embedded in amorphous SiO$_2$ matrix (for concentrations around 50 % Si).

The conduction properties of both PS and Si/SiO$_2$ films are mainly determined by their nanostructure, i.e. by the quantum confinement of the carriers into the nanocrystals. For the nanodots, the Coulomb blockade is also significant. This allows a good description of these phenomena by means of a quantum confinement model.

The bright PL in the visible range of nc-Si is a result of both quantum confinement and surface/interface effects. The maximum position shifts to higher energy when the nanocrystal sizes decrease. In Si/SiO$_2$ nanocomposites, the PL disappears when the Si concentration surpasses the percolation threshold.

REFERENCES