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Effect of annealing atmosphere on the structure and luminescence of Sn-implanted SiO₂ layers

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Sn nanoclusters are synthesized in 180 nm SiO₂ layers after ion implantation and heat treatment. Annealings in N₂ ambient at high temperatures ($T \geq 700^\circ\text{C}$) lead to the formation of Sn nanoclusters of different sizes in metallic and in oxidized phases. High-resolution transmission electron microscopy (TEM) analyses revealed that the formed larger nanoparticles are composed by a Sn metallic core and a SnO_x shell. The corresponding blue-violet photoluminescence (PL) presents low intensity. However, for heat treatments in vacuum, the PL intensity is increased by a factor of 5 and the TEM data show a homogeneous size distribution of Sn nanoclusters. The low intensity of PL for the N₂ annealed samples is associated with Sn oxidation. © 2005 American Institute of Physics. [DOI: 10.1063/1.1849855]

The discovery of luminescence in porous Si¹ has promoted a significant amount of effort focused on the production of nanostructured silicon-based materials with potential application in optoelectronic devices. Among the different approaches, several studies have used ion implantation of group IV elements in SiO₂ and heat treatment to obtain nanostructures exhibiting photoluminescence (PL). The observed intense visible and UV PL from Ge- and Sn-implanted silicon oxides reported by various authors was associated with oxygen deficiency centers created during the implantation and annealing processes.^{2,3} It is also well established that the annealing steps lead to the redistribution of the implanted atoms and to nanocluster formation.^{2–6} In a recent study, Spiga *et al.*,⁴ using x-ray absorption spectroscopy and Mössbauer spectroscopy analyses, have shown that Sn-implanted SiO₂ films annealed in N₂ atmosphere lead to the formation of oxidized and metallic nanoclusters, showing a rather complex microstructure evolution in terms of distinct phases and size distribution of the nanoclusters.

In the present contribution we show that the structural evolution of the Sn nanocluster system can be tailored by the characteristics of the annealing atmosphere. Our results show that vacuum annealing produces a very uniform particle size distribution and enhances the blue-violet PL intensity of the system. These results are discussed in terms of oxidation reaction suppression taking place during the vacuum annealing.

SiO₂ films 180 nm thick were thermally grown on crystalline Si (100) substrates in a dry ambient at 1000 °C. These films were implanted at room temperature with 200 keV Sn⁺ ions and fluence of $1.5 \times 10^{16} \text{ cm}^{-2}$ corresponding to a Gaussian-type Sn concentration-depth profile with a peak concentration of about 3 at. % formed at a depth of $\approx 90 \text{ nm}$

in the oxide. Postimplantation annealings were performed in the 400–900 °C temperature range by conventional furnace processing in N₂ flux (99.998% pure) or in vacuum ($p \leq 2 \times 10^{-7} \text{ mbar}$) for 30 min. The concentration-depth distribution profiles of the Sn atoms were determined by Rutherford backscattering spectrometry (RBS). The Sn nanoclusters structural evolution was observed via cross-sectional TEM. Finally, the PL measurements were performed at RT using excitation energy of 5 eV from a Xe lamp. All spectra were corrected for the Xe-lamp spectrum, interference effects, and photomultiplier sensitivity.

Figure 1(a) shows the PL spectra of Sn-implanted SiO₂ layers annealed in N₂ ambient and in vacuum for different temperatures. The spectra consist of a blue-violet emission peak around 3.18 eV, which is accompanied by a weaker emission in the UV spectral region ($\approx 4.15 \text{ eV}$). For the N₂ annealed samples, the PL intensity of the blue-violet emission increases with temperature up to 600 °C and then strongly decreases. This situation contrasts with the much higher blue-violet PL intensity observed from samples annealed in vacuum in the 700–900 °C temperature range [Fig. 1(b)]. The results also reveal that the PL emissions remain unshifted in energy and no significant change in the full width at half maximum is observed as a function of temperature. This agrees with other PL data,^{2,3} and means that quantum confinement effects for Si, Ge, and Sn nanoclusters can be excluded as a main mechanism of origin of the blue-violet and UV PL bands. Similar to the Ge-implanted SiO₂ layers, the intense blue-violet and UV PL from Sn-implanted SiO₂ layers are also attributed to neutral oxygen vacancy (NOV) luminescence centers, with $\equiv\text{Sn}-\text{Sn}\equiv$ or $\equiv\text{Sn}-\text{Si}\equiv$ structures formed within the SiO₂ layer.²

In order to understand these PL results, it seems important to investigate the characteristics of the obtained microstructure as a function of the annealing process (N₂ atmosphere or vacuum). Figure 2 displays the cross-sectional TEM images showing the structural evolution of the Sn

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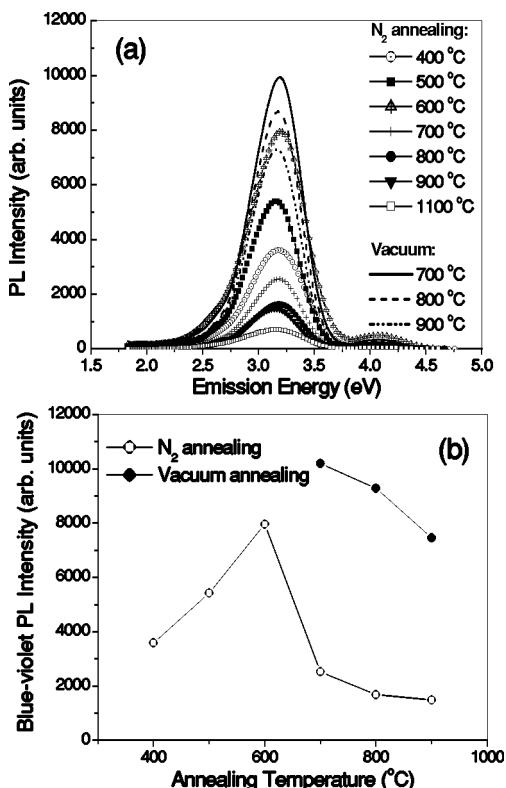


FIG. 1. (a) PL spectra of Sn-implanted SiO₂ layers after annealing in N₂ ambient and in vacuum at different temperatures. (b) Blue-violet PL peak intensity for the Sn-implanted SiO₂ layers annealed in N₂ ambient (open circle) and in vacuum (closed circle).

nanocluster system for annealing in N₂ atmosphere. The solid line gives the redistribution of Sn atoms obtained by RBS measurements. While for temperatures up to 600 °C the formed Sn nanocluster band is centered in the peak region of the Gaussian-type RBS profile [Fig. 2(a)], with increasing temperature, an evident structural evolution is observed. At 700 °C [Fig. 2(b)], the formation of a near-surface nanocluster band with small particles of mean diameter $\langle d \rangle = 2.2$ nm

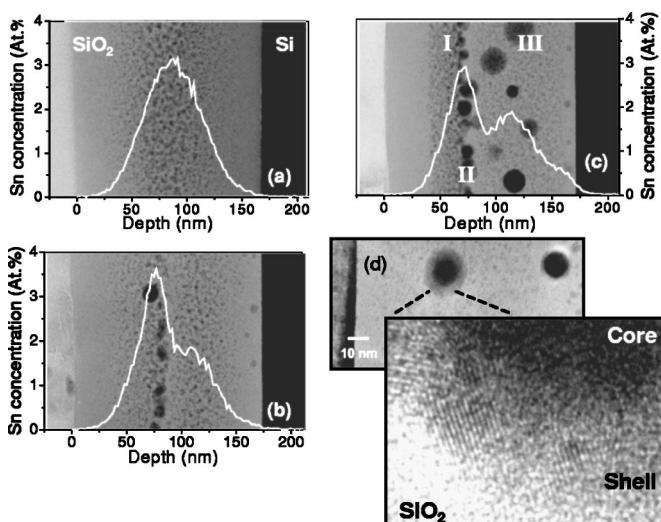


FIG. 2. Cross-sectional TEM images showing the Sn nanoclusters within the SiO₂ layer after heat treatment in N₂ ambient at 600 °C (a), 700 °C (b), and 900 °C (c) and (d). The solid lines give the Sn distribution profile obtained by RBS. The inset of (d) displays a lattice image of a particle formed by a β-Sn core and a SnO_x shell.

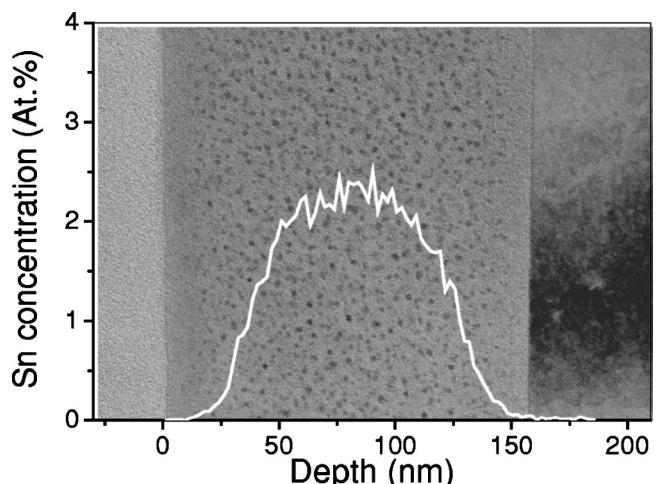


FIG. 3. Cross-sectional TEM image showing the Sn nanoclusters within the SiO₂ layer after heat treatment at 900 °C in vacuum. The solid line gives the Sn distribution profile obtained by RBS.

takes place. At 900 °C [Fig. 2(c)], the size evolution is more pronounced and the nanocluster system shows a rather complex configuration, which can be characterized in terms of three distinct regions. Region I is located near the oxide surface and contains a rather high concentration of small clusters. Region II shows a narrow distribution of larger clusters. Region III extends from region II to the SiO₂/Si interface and contains very large clusters coexisting with a high density of smaller ones. Although the heat treatments were performed under a pure N₂ flux (99.998% pure), the existence of O₂ or H₂O is expected. In addition, a backstream contamination effect from the annealing system can also occur. Hence, the formation of the near-surface nanocluster band (region I) is probably related to the diffusion of Sn atoms from the middle of the SiO₂ layer toward the surface, where they meet the indiffusing oxygen present in the N₂ annealing ambient, thus favoring the formation of small SnO_x nanoparticles in this region. The microstructure shown in Fig. 2 has been typically obtained by other authors after annealing in dry N₂ atmosphere, observing also contamination-related SnO_x clusters.^{4,5}

In addition, we have observed the formation of large two-phase Sn nanoclusters in the SiO₂ layer, constituted by a core and a shell [see Fig. 2(d)]. The core shows a strong contrast, which can be attributed to a β-Sn metallic phase. The inset of Fig. 2(d) shows that the shell is composed of polycrystalline SnO_x, as characterized by the lattice fringe images.

As opposed to the N₂ annealing case, Fig. 3 shows that the formed nanoclusters for vacuum annealing at 900 °C are much more homogeneously distributed in depth along the SiO₂ layer and present a size distribution with mean diameter $\langle d \rangle = 2.5$ nm and a small dispersion given by a standard deviation of 0.5 nm. Moreover, for the vacuum annealed specimen the flat depth-concentration profile given by RBS measurement shows a redistribution of the Sn atoms over the entire SiO₂ layer. This redistribution is probably due to the absence of the trapping centers, allowing the Sn diffusion from the original as implanted Gaussian-type profile toward the surface and the SiO₂/Si interface. As a consequence, we do not observe either the formation of a distinct SnO_x-related band close to the surface or the coexistence of large particles

in deeper regions. Finally, it is important to remark that the RBS measurements show that the total implanted Sn content is conserved after annealing in N₂ or vacuum.

Therefore, the obtained TEM results suggest that the formation of SnO_x phases within the SiO₂ matrix, after N₂ ambient heat treatments in the 700–900 °C temperature range, is the reason for the reduction of the blue-violet PL intensity. In our recent studies for Ge-implanted SiO₂ layers,³ we have investigated the coarsening of Ge nanoclusters and its relation with the blue-violet PL intensity. For high anneal temperatures (900 °C), a significant fraction of Ge atoms (≈ 25 at. %) are not located in the Ge nanoclusters, but possibly trapped in the form of NOV luminescence centers with \equiv Ge–Ge \equiv or \equiv Ge–Si \equiv structures distributed around the nanoclusters. Hence, for the present Sn–SiO₂ system, during the annealing in the N₂ atmosphere, the O₂ or H₂O contamination leads to the oxidation of the Sn and to the formation of SnO_x small clusters or SnO_x shells around the large Sn clusters. This effect reduces the number of Sn atoms present in solution, decreasing the formation of NOV centers with \equiv Sn–Sn \equiv or \equiv Sn–Si \equiv structures distributed around the nanoclusters and strongly affecting the PL intensity. On the other hand, for the vacuum annealed samples the absence of oxygen contamination during the heat treatment minimizes the Sn oxidation, leading to a high fraction of Sn atoms forming NOV centers around the Sn nanoclusters and enhancing the PL intensity.

In summary, from the study of the Sn nanoclusters structural evolution in Sn-implanted SiO₂, important information is obtained about the oxidation of Sn atoms and its relation to the PL emission intensity. The PL behavior is demonstrated to be inconsistent with quantum confinement effects and is attributed to \equiv Sn–Sn \equiv or \equiv Sn–Si \equiv NOV light-emitting centers. The large decrease of PL intensity for the N₂ annealed samples is attributed to the SnO_x clusters and SnO_x shells formed around the Sn nanoclusters, which prevent the creation of the NOV centers around the nanoclusters. Moreover, we have observed that the vacuum annealing prevents the Sn oxidation and leads to the formation of homogeneously size distributed Sn nanoclusters and to the improvement of the blue-violet PL intensity, which can be of great importance for applications in Si-based optoelectronic devices.

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