EPR and emission study of silicon suboxide nanopillars

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ABSTRACT

The results of correlated electron paramagnetic resonance (EPR) and photoluminescence (PL) study of obliquely deposited porous SiOₓ films after step-by-step 15 min annealing within 105 min in vacuum at 950°C are presented. The low intensity symmetrical and featureless EPR line with a g-value g=2.0044 and a linewidth of 0.77 mT has been detected in as-sputtered films and attributed to dangling bonds (DB) of silicon atoms in amorphous SiOₓ domains with x=0.8. Successive annealing results in decreasing this line and the appearance of an intense EPR line with g=2.0025, linewidth of 0.11 mT and a hyperfine doublet with 1.6 mT splitting. According to the parameters this spectrum has been attributed to the EX center, a hole delocalized over four non-bridging oxygen atoms grouped around a Si vacancy in SiO₂. The impact of chemical treatment before annealing and duration of anneals on the defect system, and a correlation of the PL intensity with decreasing of the DB EPR signal are discussed.

INTRODUCTION

Owing to intense emission at room temperature, the structures consisting of Si nanocrystallites (nc-Si) embedded in silicon oxide SiO₂ or suboxide SiOₓ (1<x<2) show considerable promise for optoelectronic and photonic applications [1-4]. To the fabrication of these structures several techniques like the plasma-enhanced deposition, ion implantation, laser ablation, magnetron sputtering, evaporation in vacuum etc. are used. All these methods allow to fabricate SiOₓ films with required x. Subsequent thermally induced decomposition of a suboxide and the formation of Si nanoparticles in SiOₓ matrix are governed by a relation ySiOₓ → xSiOₓ + (y–x)Si, where y > x, and SiOₓ will be evidently consisted of SiO₂ and SiOₓ. The temperature of annealing determines the structure of inclusions: annealing below 1000°C favors a coalescence of Si atoms into amorphous clusters, at higher temperature silicon nanocrystals are formed [1-5].

Thermally induced formation of nc-Si results in considerable dispersion of nanocrystallite sizes, that in turn decreases the intensity of photoluminescence (PL) and increases the half-width of PL band. Recently it has been shown that thermal evaporation of silicon monoxide on a substrate obliquely oriented to direction of evaporated substance stream and subsequent annealing in vacuum lead to the formation of porous SiOₓ films with columnar structure and nc-Si inclusions (see [6, 7] and references there). Depending on the angle of evaporation and other technological parameters the diameter of deposited columns varies from 10 to 100 nm. Limited volume of SiOₓ columns results in smaller dimensions of nc-Si than ones in normally deposited dense films with the same x. Relatively high porosity of obliquely deposited films makes it possible to control their light-emitting properties. The dependences of PL band position on pre-annealing chemical treatment in ammonia or acetone saturated vapor [8], on selective etching of nc-Si/SiOₓ structures in HF solution [7] and on post-annealing chemical treatment in HF and H₂O₂ vapors [9] have been recently observed.
In above-mentioned publications [6-9] the obliquely deposited films were studied mainly with optical methods. The temperature of anneals in vacuum was restricted to 950-975°C to avoid the process of film sublimation and the duration of thermal annealing was limited to 15 minutes. Electron paramagnetic resonance (EPR) is an indispensable tool for the defect identification in crystalline and amorphous materials; it is well suited for a quantitative study of volume and surface defects. Studying with EPR the normally deposited dense SiO_x films it has been shown that paramagnetic defects and their evolution may reflect the structural transformations of films [2]. Annealing duration was found an important parameter for properties of nc-Si/SiO_x structures in dense films [2, 10]. This work is aimed to elucidating the basic types of paramagnetic defects and their evolution during thermal annealing of obliquely deposited films. The results of correlated EPR and PL study of porous SiO_x films after step-by-step 15 min anneals within 105 min in vacuum at 950°C are presented.

EXPERIMENT

Thin (about 960 nm) SiO_x films were deposited by thermal evaporation of silicon monoxide SiO (Cerac Inc.) in vacuum (1±2) × 10^{-3} Pa on polished (100) Si substrates arranged at an angle β=75° between the normal to the substrate surface and the direction of an evaporator. Step-by-step 15 min anneals within 105 min were carried out in a vacuum chamber at 950°C and a residual pressure of 1×10^{-3} Pa. Three types of samples labeled las, lam and lac were annealed simultaneously. Samples of the las group represented as-deposited untreated films, while samples of the lam and lac groups were kept during 120 hours in ammonia and acetone saturated vapor before the first anneal, respectively.

The EPR measurements were carried out at 300 K using an X-band (ν = 9.32 – 9.54 GHz) spectrometer with a lock-in signal detection at the magnetic field modulation frequency of 100 kHz. Signal averaging facilities were used to measure low intensities and linewidths without overmodulation and saturation effects. Amount of paramagnetic defects was determined relative to a MgO:Mn^2+ standard sample with a known number of spins through double numerical integration of the respective derivative absorption signal. The g-values were determined with a precision of Δg = ± 0.0001 via a microwave frequency counter and a calibration of the magnetic field by a proton nuclear magnetic resonance probe.

The photoluminescence spectra of SiO_x samples were measured at room temperature using a MDR-23 grating spectrometer with a cooled FEU-62 photomultiplier and a lock-in registration system. The discrete line 488 nm of an Ar ion laser and the line 532 nm of a light-emitting diode were used for excitation.

A scanning electron microscope (SEM) Zeiss EVO 50XVP was used to observe the cross-section of deposited films.

RESULTS and DISCUSSION

A typical cross-sectional view of SiO_x film obliquely deposited at β=75° on silicon wafer is shown in figure 1. As can be seen in the figure, the investigated SiO_x films have a porous inclined pillar-like structure with the pillar diameters of 10-100 nm. The porosity of films depends on the angle at the deposition and equals to 53% for β=75°. High-temperature annealing of these films does not change the porosity and pillar-like structure of samples.
Figure 1. The SEM micrograph of SiO\textsubscript{x} film cross-section for a sample deposited at \(\beta=75^\circ\).

EPR spectra were found to be identical for unannealed samples of all three groups, for the Ias group of SiO\textsubscript{x} films they are shown in figure 2a. Before annealing the samples are characterized by a broad structureless EPR line with \(g\)-value of 2.0044±0.0002 and width \(\Delta B_{pp}=0.77\) mT.

Figure 2. \(a\) – Room temperature EPR spectra for the Ias group of SiO\textsubscript{x} films before (0) and after annealing at 950°C for 15 (1), 30 (2), 75 (3) and 105 (4) min, microwave frequency \(\nu=9.442\) GHz; intensities of spectra are normalized to unit sample area. \(b\) – Hyperfine doublet of the \(EX\) center detected on an Iac sample after anneals for 105 min, \(\nu=9.515\) GHz, \(T=300\)K.
Its slightly asymmetric line shape indicates that the spectrum may be a superposition of several components, the parameters are close to those of the EPR line observed in amorphous SiO$_x$ films with $x \approx 0.8$ [11]. This line can be attributed to dangling bonds (DB) of Si atoms in structural tetrahedrons Si–Si$_2$O and, probably, in amorphous Si precipitates [2]. On the assumption of a uniform distribution of paramagnetic centers across the film thickness, their volume density is found to be $1.5 \times 10^{19}$ cm$^{-3}$. Notice that due to optical measurements the main body of as-deposited porous SiO$_x$ films corresponds to $x \approx 1.5$ [6, 7].

Annealing of the films studied gives rise to a narrow EPR line with $g = 2.0025 \pm 0.0001$ and $\Delta B_{pp} = 0.10$ mT, its intensity increases considerably with prolongation of annealing time while the DB line drops (figure 2a). Measurements on a sample with the greatest intensity of the narrow line provided a possibility to reveal its hyperfine doublet with $1.60$ mT splitting (figure 2b). The observed parameters of EPR line are characteristic of so-called the EX center – a specific defect in SiO$_2$ pictured as a hole delocalized over 4 nonbridging oxygen atoms grouped around a Si vacancy [12]. It is pertinent to note that the hyperfine structure of the EX center in SiO$_2$ has been previously observed mainly at 4.2K [12, 13], for nanometer-sized silica particles it has been revealed at 100K [14]. To the best of our knowledge, hyperfine doublet of the EX center has been distinctly recorded at room temperature for the first time.

Chemical treatment in acetone and ammonia vapor before thermal annealing of porous SiO$_x$ films furnishes different results. The density of paramagnetic defects in acetone-treated samples is comparable to that of untreated ones while for ammonia-treated samples it is three times less (figure 3). We believe that hydrogen atoms arising by ammonia dissociation can passivate a considerable amount of the DB defects.

![Figure 3.](https://www.cambridge.org/core/40d96a8a89224e158b3e54b70454b70e)

Figure 3. EPR spectra for the lac (a) and lam (b) groups of SiO$_x$ films before (0) and after annealing at 950°C for 15 (1), 30 (2), 75 (3) and 105 (4) min, $\nu = 9.442$ GHz, $T = 300$K, intensities of spectra are normalized to unit sample area.

Transformations with annealing of EPR spectra for the lac group is similar to the las one with the exception of higher growing of the EX line. Contrary to them, relatively intense EX line appears after the first anneal for 15 min of samples of the lam group remaining practically
unchanged after the following annealing steps (figure 3b). Comparing the total number of paramagnetic defects before and after annealing for 105 min, about fourfold decrease of them was found for all groups.

Simultaneously with decreasing of defect amounts a rise of PL intensity has been observed for all groups of samples, for the Ias group it is presented in figure 4a.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Room temperature PL spectra:  
- **a** – for a sample of the Ias group after annealing at 950°C for 15 (1), 30 (2), 75 (3) and 105 (4) min, λ_{exc} = 532 nm;  
- **b** – for samples of different groups of SiO_x films annealed at 950°C for 15 min, λ_{exc} = 488 nm.

Overall, the gain of integral PL intensity correlates with reduction in the number of DB centers. Defects of the dangling bond type are usually considered as non-radiative recombination centers. In any case, optically-detected magnetic resonance technique must be used to elucidate their role since a variety of non-paramagnetic defects can be annealed simultaneously with paramagnetic ones. Qualitatively, the increase of PL intensity can be explained by the passivation of non-radiative recombination centres at nc-Si/SiO_x interface [15].

Excitation with 488 nm provides a way for observation of new short wavelengths PL bands for chemically treated samples (figure 4b). It is assumed that nitrogen in ammonia and carbon in acetone promotes passivation of nc-Si surface by nitrogen or carbon and prevents formation of Si=O bonds during annealing in vacuum and further exposure on air. Moreover, the presence of acetyl and methyl influences on oxidation (or oxicarbonization) of silicon and formation of nc-Si with smaller sizes takes place [16].

Comparing the EPR results of present study with those obtained on normally deposited dense SiO_x films [2] we can find several main distinctions. First, for as-deposited dense films (where x ≈ 1.3) the volume defect density was estimated as 4 × 10^{20} cm^{-3}, that is an order of magnitude higher than for porous films. Evidently, this is a direct consequence of higher value of x for the latter films. Second, thermal annealing of dense SiO_x films at 900°C gave rise to the emergence of EPR line with g = 2.0055, typical for dangling bonds in amorphous Si precipitates. The lack of this signal in EPR spectra of porous films implies smaller concentration of Si nano-
crystallites there. Third, the EX center has never been observed in dense SiO$_x$ films, it is due to porosity of obliquely deposited films that promotes oxidation of pillars surface.

CONCLUSIONS

An EPR study of obliquely deposited SiO$_x$ films reveals the presence of the DB and EX paramagnetic centers there. The emergence of these defects and their behavior with thermal annealing furnish important information about the structural peculiarities of the films. The impact of chemical treatment before annealing and the duration of anneal on the defect system, and a correlation of the PL intensity with decreasing of DB EPR signal have been observed.

REFERENCES