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Effects of chemical stoichiometry on the structural properties of Si-rich oxide thin films

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ABSTRACT

In this work, the various chemical stoichiometry (O/Si ratios) of silicon-rich SiO_2 (SRO) thin films were deposited and then annealed by rapid thermal annealing (RTA) to form SiO_2-matrix silicon nanocrystals (Si–NCs). The effects of the O/Si ratios on the structural properties of SRO thin films were investigated systematically using Raman spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Results showed that the micro-structure of as-deposited SRO thin films with higher O/Si ratios hindered formation of Si–Si_4 clusters, Si clusters and Si rings, then hindered the phase separation and the crystallization of annealed thin films. When the O/Si ratios was increased from 0.7 to 1.5, the crystalline temperature was increased from 900 °C to 1000 °C, the crystalline fraction of the 1000 °C-annealed thin films was reduced from 39.4% to 22.7%, the average Si–NC size was reduced from 3.8 nm to 3 nm, and the residual stress was increased from 1.9 GPa to 2.8 GPa, respectively. The changes in micro-structure were most possibly due to the fact that the different amount of Si-O bonds in the as-deposited thin films with various O/Si ratios.

1. Introduction

Silicon nanocrystals (Si–NCs) embedded in SiO_2 matrix are widely considered as a promising material for potential applications in the fields of optoelectronics [1], photovoltaics [2], and single electron devices [3,4]. Depositing silicon-rich SiO_2 (SRO) thin films with subsequent high-temperature annealing is one of the most popular methods for preparing Si–NC thin films [5,6]. Hong *et al.* [7] reported that the Si–NC thin films possessed higher crystalline fraction and larger average Si–NC size with the increased of annealed temperature. The formation of Si–NCs in the annealed thin films usually includes the phase separation of SRO thin films and the crystallization of Si phase. The annealing temperature has significant impacts on the properties of the annealed SRO thin films [8].

The phase separation, crystallization properties and optical properties of Si–NC thin films depend not only on the annealing process, but also on the properties of as-deposited SRO thin films [9–12]. Iwayama *et al.* [13] reported that the structural properties of Si–NC thin films depend on the excess Si concentration and annealing temperature. The chemical stoichiometry (O/Si ratios) of the SRO thin films is widely regarded as a main parameter to control the Si–NC size, the density of the Si–NCs and crystalline fraction of annealed SRO thin films [14–16]. Hao *et al.* [14] reported that the crystallization of Si phase was suppressed and the Si–NC size was significantly reduced with the increased of O/Si ratios. The network structure order of the as-deposited SRO thin films were enhanced with the increased of O/Si ratios [17,18]. Andrés *et al.* [18] reported that the higher O/Si ratios would hinder phase separation of SRO thin films during the subsequent high-temperature annealing. The micro-structure of the higher O/Si ratios thin films will facilitate the formation of larger density of extended defects and high surface-to-volume ratio of the thin films [19]. Hao *et al.* [20] found that the photoluminescence intensity of the thin films was decreased and the absorption edge blue-shifted with the increased of O/Si ratio.

It is well known that the O/Si ratios have significant impacts on the properties of the as-deposited and annealed SRO thin films. In the previous studies, the effect of O/Si ratios on the structural properties of thin films was mostly studied in terms of structural order of the as-deposited SRO thin films and structural properties of annealed thin films only. Considering the strong dependence of both the density and size on the various O/Si ratios of SRO thin films, it is necessary to investigate how and why the O/Si ratios influences the structural properties of the as-deposited and annealed thin films [9,12,13]. In this work, the effects of O/Si ratios on the structural properties of as-deposited and annealed SRO thin films were investigated systematically. In this work, various O/Si ratios of SRO thin films were deposited and annealed using rapid thermal annealing (RTA). The effects of O/Si ratios on

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the structural of as-deposited and annealed SRO thin films were investigated systematically using Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental details

The SRO thin films were deposited on double-sided polished silicon and quartz substrates by magnetron co-sputtering of silicon target (4 in.) and silicon dioxide targets (4 in.) using a multi-target magnetron sputtering system (JSputter-8000, ULVAC) at room temperature. The substrates were cleaned by ultrasonic baths of acetone and distilled water for about 60 min each. The double-sided polished silicon substrates were dipped in a dilute (5%) HF solution for removal of the surface native oxide. Upon achieving a base pressure of 1.5×10^{-8} Torr, argon (Ar) was introduced to the chamber for a working gas pressure of 1.5×10^{-3} Torr. The O/Si atomic was controlled by adjusting the power applied to the Si and SiO_2 targets, respectively. The thickness of the thin films was ~400 nm, determined by the profilometer (Veeco Dektak150). The composition of the as-deposited SRO thin films were ~$SiO_{0.7}$, $SiO_{1.0}$, $SiO_{1.2}$, $SiO_{1.3}$ and $SiO_{1.5}$, respectively, measured by XPS (Shimazu, AXIS ULTRADLD). The XPS measurements were carried out after a 120 s Ar ion sputter etch to remove surface oxidation. The Ar ion bombardment etching rate was approximately 2.0 Å/s. The XPS spectrawere calibrated by using the C 1 s peak (284.5 eV). Integrated area intensities under the O1s and Si2p peaks in conjunction with core level atomic sensitivity factors were used to estimate the relative elemental composition of the films. After deposition, the SRO thin films were annealed using RTA at 900 °C and 1000 °C for 120 s in Ar ambient.

The chemical composition and the rings information was studied by FT-IR (Thermo, NICOLET 6700) in the spectral range between 400 and 1400 cm^{-1} with a resolution of 1 cm^{-1}. High resistivity (>1000 cm^{-1}) and double-sided polished silicon wafers were used as substrates. The chemical structure of thin films was also measured by XPS. The Si clusters information and the crystalline fraction of thin films was carried out using confocal micro-Raman spectroscope (Renishaw, InVia-Reflex) with Ar laser (532 nm). Here, the sample was measured three times in different areas, the average value was chosen, and the root mean square was used as the error bar. The Raman spectra were decomposed into three components: the Si–NCs peaked at 510–520 cm^{-1}, the amorphous Si peaked at 480 cm^{-1}, and an intermediate component peaked at 500–510 cm^{-1} [21]. The crystalline fraction is calculated using the following equation [21,22]:

$$X_c = (I_c + I_m)/(I_c + I_m + yI_a) \quad (1)$$

where I_c, I_a, and I_m denote the integrated intensities of the Si–NC, amorphous, and intermediate peaks; y is the ratio of the integrated Raman cross-section and equals to 1 due to the small Si-NC size.

The compressive and tensile stresses cause only redshift and blueshift of Si–NC peak position. The full width at half maximum (FWHM) of Si–NC peak is almost insensitive to the thin-film stress [21–24]. The position and FWHM of Si–NC peak is affected by the small-size Si–NCs and residual stress [22,23]. The residual stress and average Si–NC size can be calculated as follows [22]:

$$\Delta\omega(D) = -97.462(0.543/D) \quad (2)$$

$$\mathrm{FWHM}/2 = (D + 3.1309)/(0.81004D - 1.6053) \quad (3)$$

$$\sum = \Delta\omega/1.88 \quad (4)$$

where D is the average Si–NC size, $\Delta\omega$ is the Raman peak shift and $\sum$ is the Si–NC stress. The average Si–NC size is calculated from the FWHM of Si–NC peak using Eq. (3), then the peak redshift arising from Si–NCs is derived from Eq. (2). The stress can be calculated from the remaining peak shift using Eq. (4).

3. Results and discussion

Fig. 1 shows the XPS spectra of Si 2p and O 1 speaks of as-deposited SRO thin films with various O/Si ratios. It was observed that the Si 2p peak was fitted into five chemical states, corresponding to Si^0 (99.3 eV), Si^{1+} (100.3 eV), Si^{2+} (101 eV), Si^{3+} (101.9 eV), and Si^{4+} (103.3 eV) [9,25], the O 1 s peak was fitted into two chemical states: O^{2-} the one in $Si–O_4$ clusters (532.6 eV) and $O^{4/x-}$ in $Si–Si_x–O_{4-x}$ ($1 \le x \le 3$) clusters (<532.6 eV), respectively [26–28], as shown in Figs. 1(a) and (b). The peaks of Si^{4+} and O^{2-} were weak in the $SiO_{0.7}$ thin films, whereas the peaks of Si^0 and $O^{4/x-}$ were intensive, which indicated that most of the $Si–Si_4$ clusters and $Si–Si_x–O_{4-x}$ ($1 < x < 3$) clusters were in the thin films. The peaks of Si^{4+} and O^{2-} were more clearly resolved and enhanced in intensity with the increased of O/Si ratios, which indicated that most of the $Si–O_4$ were in the thin films. In addition, the O1s peak becomes broader with the decreased of O/Si ratios. The results indicated that the amount of $Si–Si_x–O_{4-x}$ ($1 < x < 3$) clusters gradually increased which due to the electronegativity of the O atoms in $Si–Si_x–O_{4-x}$ ($1 < x < 3$) clusters below the one in $Si–O_4$ clusters.

Fig. 2(a) shows the FT-IR spectra of as-deposited SRO thin films with various O/Si ratios. The peaks at about 460, 808, 880, 1000–1100 cm^{-1}, characteristic of silicon oxide films, are due to the O–Si–O rocking, Si–O–Si bending, Si rings configurations isolated by oxygen atoms, and Si–O–Si asymmetrical stretching vibrations, respectively [29]. It was observed that the intensity of the peak at 880 cm^{-1} decreased when the O/Si ratios increased from 0.7 to 1.5. The results indicated that the Si-ring

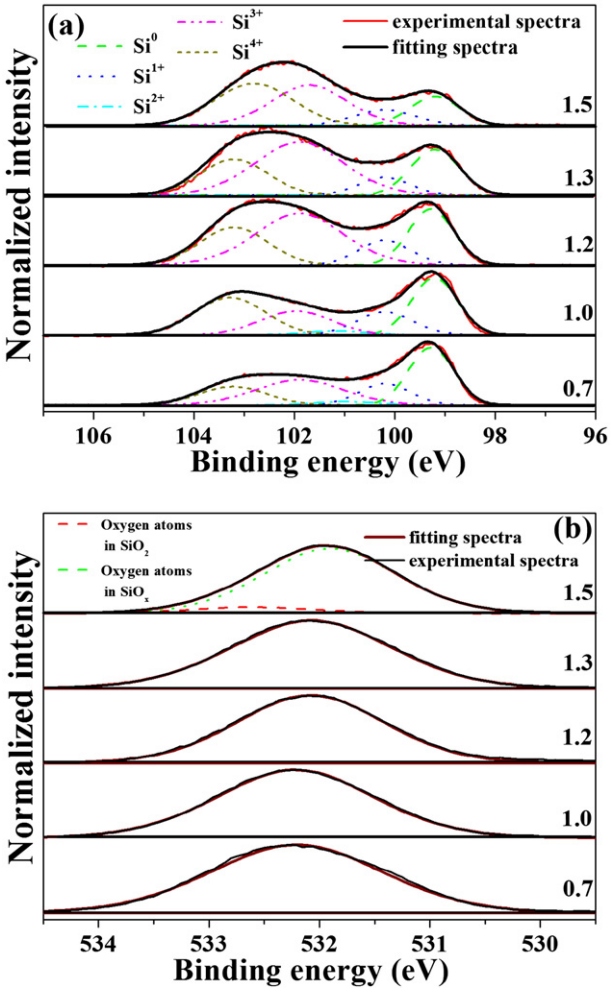

Fig. 1. The Si 2p (a) and O 1 s (b) XPS spectra of as-deposited SRO thin films with various O/Si ratios.