In situ characterization of stoichiometry for the buried SiO$_{x}$ layers in SiO$_{x}$/SiO$_2$ superlattices and the effect on the photoluminescence property

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Abstract

The stoichiometry of SiO$_x$ layers in SiO$_x$/SiO$_2$ superlattice (SL) films grown by ion beam sputtering method was determined with in situ X-ray photoelectron spectroscopy. The effect of oxygen content on the photoluminescence (PL) properties was studied for the bulk-SiO$_x$ films and SiO$_x$/SiO$_2$ SLs. Maximum PL intensities were observed near $x \approx 1.6$ and $x \approx 1.2$ for the bulk-SiO$_x$ films and SiO$_x$/SiO$_2$ SLs, respectively. However, the dependence of PL intensity and energy on the film stoichiometry, when scaled for the overall film stoichiometry, was nearly the same for the bulk-SiO$_x$ films and SiO$_x$/SiO$_2$ SLs. This result indicates that the oxygen content is the main parameter to determine PL property of the SiO$_x$/SiO$_2$ SLs.

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1. Introduction

It is well known that SiO$_2$ embedded with Si nanocrystals (Si-ncs) can act as a source of visible light emission. Many different methods have been used to fabricate such films (e.g., Si ion implantation into SiO$_2$ [1,2], reactive evaporation of SiO [3,4], plasma-enhanced chemical vapour deposition [5–7], radio frequency co-sputtering of Si and SiO$_2$ [8]). Nowadays, a lot of attention has been focussed on increasing the photoluminescence (PL) energy and enhancing the PL intensity for the device applications, particularly by controlling the size and density of Si-ncs. Recently, it was reported that such control is possible by using SiO/SiO$_2$ superlattices (SLs), as evidenced by a strong blue shift of PL peak from 960 to 810 nm as the SiO layer thickness was reduced from 3.8 to 2.0 [4]. They showed that the position and size of Si-ncs can be controlled by constructing superlattice structures of SiO and SiO$_2$ layers. However, a comprehensive investigation of the effects of stoichiometry of the SiO$_x$ layers in SiO$_x$/SiO$_2$ SLs on their PL properties is so far lacking, even though the stoichiometry is an important parameter that determines the PL properties. Furthermore, a comparison between bulk SiO$_x$ films and SiO$_x$/SiO$_2$ SLs that are necessary for a more complete and precise understanding has not yet been reported.

In this paper, we report on the characterization method of the stoichiometry of SiO$_x$ layers in SiO$_x$/SiO$_2$ SLs and the effect on the luminescence properties of SiO$_x$/SiO$_2$ SL deposited by ion beam sputter deposition (IBSD) method. IBSD is a good candidate for the growth of SiO$_x$ films due to its capability for low-temperature growth of Si and SiO$_2$ thin films [9–11]. And the film growth at low growth temperatures can result in a great enhancement of the nc-Si luminescence [7]. Furthermore, by using IBSD, it is possible
to control the individual layer thicknesses with sub-nm precision. We found that the PL peak position can be tuned by varying the Si content of the SiO$_x$ layers. The dependence of the PL intensities from bulk SiO$_2$ films and SiO$_x$/SiO$_2$ SLs on the SiO$_x$ stoichiometry was found to be different, with maximum PL intensities occurring near $x \approx 1.6$ and $x \approx 1.2$, respectively. However, the stoichiometry dependence, when scaled for the overall film stoichiometry, was nearly the same between the bulk SiO$_2$ and SiO$_x$/SiO$_2$ SL films. This indicates that the PL property of the SiO$_x$/SiO$_2$ SLs with very thin layer thickness depends on the averaged oxygen content of the two layers.

2. Experimental methods

SiO$_x$/SiO$_2$ superlattice thin films with 50 periods of 2-nm-thin layers were grown by reactive ion beam sputtering deposition using a Kaufman type DC ion gun and an Ar$^+$ beams with ion energy of 750 eV. Si atoms sputtered from a Si target by sputtering with Ar$^+$ ion beams were deposited on p-type Si (100) wafers at room temperature under oxygen atmosphere. Oxygen partial pressures were switched for the SiO$_x$ and SiO$_2$ layers. A mass flow controller (MFC) and a needle valve were used to control oxygen pressure. Initially, low oxygen pressures between 2.0 and $9.3 \times 10^{-5}$ mbar were fixed by the needle valve to grow SiO$_x$ layers and then the MFC valve opened and adjusted to a pressure of $2.1 \times 10^{-4}$ mbar to grow SiO$_2$ layers. In this condition, SiO$_x$ layers were grown by turning-off the MFC valve and SiO$_2$ layers were grown by turning-on the MFC valve. The switching time between the two layers was very short. Carbon and any other contaminants were not found on the film surfaces by in situ X-ray photoelectron spectroscopy (XPS) analysis. The relative film thickness was controlled from the growth rate calibrated by transmission electron microscopy measurement of films grown within a given time. The deposition chamber was evacuated to a pressure of $2.7 \times 10^{-8}$ mbar by a turbo molecular pump before introducing argon gas into the system. Details of the system are described elsewhere [12]. The relative oxygen content was controlled by varying the oxygen gas pressure. Bulk, single-layer SiO$_x$ thin films of 80 nm thickness were also deposited under identical conditions for comparison with the SLs. The stoichiometry of the SiO$_x$ films was analysed and controlled with in situ XPS using Al $k\alpha$ line of 1486.6 eV. A stoichiometric SiO$_2$ thin film was used as a reference for the determination of the relative sensitivity factors of Si 2p and O 1s peaks.

3. Results and discussions

In order to study the effect of oxygen content on the PL properties of SiO$_x$/SiO$_2$ SLs, a quantitative analysis of silicon and oxygen atoms in the buried SiO$_x$ layers is required. However, in situ control of the oxygen content of SiO$_x$ layers in SiO$_x$/SiO$_2$ SL films is somewhat difficult to determine because the SiO$_x$ layer can be more oxidized during the period of switching oxygen partial pressures for the SiO$_2$ and SiO$_2$ layers. This additive oxidation effect on the SiO$_x$ layers increase severely as the layer thickness decrease. Therefore, the oxygen pressure must be readjusted for the growth of SiO$_x$/SiO$_2$ SL films with constant oxygen content. The XPS analysis depth of SiO$_2$ was reported to be longer than 10 nm [13]. This corresponds to more than five layers in SLs with 2-nm layer thickness. If the thickness of the SiO$_2$ and SiO$_2$ layers are the same, the stoichiometry of the individual layers can be estimated by comparing the measured average oxygen contents of SiO$_x$-terminated and SiO$_2$-terminated SiO$_2$/SiO$_2$ SLs as shown schematically in Fig. 1. Therefore, the oxygen content ($x$) of the SiO$_x$ layers in the SLs can be determined by the following simple equation because the oxygen content of the SiO$_2$ layer is 2.

$$x = X_1 + X_2 - 2$$

Here, $X_1, X_2$ are the average oxygen contents of the SiO$_2$-terminated and SiO$_2$-terminated SLs, respectively, which were measured by in situ XPS. For the correct application of this method, the effect of difference in atomic densities of SiO$_2$ and SiO$_2$ layers must be compensated. However, the formula ($X_1 + X_2 = 2 + x$) will be valid for the two SL systems with extremely thin (thinner than one atomic layer) and extremely thick (thicker than XPS analysis depth) layers. If the difference in atomic density of SiO$_2$ and SiO$_2$ layers is not too high, this validity can be extended to the SL films with intermediate thickness (2 nm). For example, for an oxygen partial pressure at $3.7 \times 10^{-5}$ mbar, $X_1, X_2$ are 1.79$\pm$0.02 and 1.05$\pm$0.02, respectively. Therefore, the oxygen content of the SiO$_x$ layers in the SiO$_2$/SiO$_2$ SL could be estimated to be 0.84 from the above equation. This value is the same as the oxygen content measured for the bulk, single SiO$_2$ single film grown under the same growth conditions. This result

![Fig. 1. Estimation of oxygen content of the buried SiO$_x$ layers in SiO$_2$/SiO$_2$ SLs by measuring average oxygen content of SiO$_2$- and SiO$_2$-terminated SiO$_2$/SiO$_2$ SLs.](image)
means that the oxidation of SiO$x$ layers during growth is negligible and thus confirming the validity of our approach.

After deposition, the samples were annealed at 1100 °C for 20 min in an ultra-pure nitrogen ambient using a horizontal furnace to form Si-ncs in the SiO$x$ layers. The samples were also hydrogenated for the passivation of the Si dangling bonds for 1 h at 650 °C under hydrogen gas flow. Photoluminescence spectra were measured using the 488-nm line of an Ar laser as the excitation source at room temperature. Emitted light was collected by a lens and analysed using a grating monochromator and a GaAs photomultiplier. Standard lock-in detection techniques were used to maximize the signal-to-noise ratio. The laser beam diameter was about 0.3 mm and the power was about 10 mW.

Fig. 2 shows the room temperature photoluminescence spectra of the SiO$_x$/SiO$_2$ SLs with different SiO$_x$ layer stoichiometry. We observed the broad PL peak in the range of 900–700 nm. The increase of PL energy from 850 nm (1.46 eV) to 770 nm (1.61 eV) as $x$ increase from 1.0 to 1.6, consistent with quantum confinement effect due to the decrease in the size of Si-ncs. This tendency of blue-shift is agreed well with previous reports on the effect of stoichiometry on nc-Si luminescence from nc-Si imbedded in SiO$_2$ matrix [14–17]. However, the maximum nc-Si PL intensity is obtained at $x=1.2$. This value is remarkably smaller than the value of 1.6 obtained from the bulk-SiO$_x$ films. This difference is clearly demonstrated in Fig. 3(a),

![Fig. 2. PL spectra of the SiO$_x$/SiO$_2$ SLs with different oxygen contents.](image-url)

![Fig. 3. Relative PL intensity (a) and energy (b) of the SiO$_x$/SiO$_2$ SLs (■) and SiO$_x$ films (○) as a function of oxygen content. By averaging the oxygen content, the plot of SLs (□) becomes similar to that of bulk SiO$_x$.](image-url)

![Fig. 4. Relative PL intensity of the SiO$_{1.2}$/SiO$_2$ (a) and SiO$_{1.6}$/SiO$_2$ (b) SLs as a function of layer thickness.](image-url)
which shows the dependence of the nc-Si PL intensity on the stoichiometry of SiO\textit{x} from both the bulk-SiO\textit{x} and SiO\textit{x}/SiO\textit{2} SLs. We can find that strong nc-Si PL is observed from bulk SiO\textit{x} films only within a narrow composition range of 1.5<\textit{x}<1.8, while strong nc-Si PL from SiO\textit{x}/SiO\textit{2} SLs can be observed in a wide composition range of 0.6<\textit{x}<1.6. However, if the SiO\textit{x} and SiO\textit{2} layers in SiO\textit{x}/SiO\textit{2} SLs are extremely thin, the entire SL structure can be regarded as a single, homogeneous SiO\textit{y} film (\textit{y}>\textit{x}). This should be true since there is no abrupt phase or structural difference between the amorphous SiO\textit{x} and SiO\textit{2} layers grown at room temperature. Furthermore, the diffusion distance of Si in SiO\textit{x} layers during annealing was reported to be as long as 3 nm \[18\]. To test this hypothesis, the nc-Si PL intensity was plotted against the average composition of the SiO\textit{x}/SiO\textit{2} SLs, as shown in Fig. 3(a). In this case, the average oxygen content (\textit{y}) of the SL can be estimated as \textit{y}=(\textit{x}+2)/2. We found a remarkable agreement between the SLs and bulk-SiO\textit{x} film with comparable average composition. Moreover, as Fig. 3(b) shows, the variation of PL energy of SiO\textit{x}/SiO\textit{2} SLs with \textit{x} also well agrees with that of the bulk-SiO\textit{y} films with comparable average composition. Again this demonstrates the meaning of the averaging effect.

To confirm the averaging effect, the effect of layer thickness was studied for the SiO\textit{x}/SiO\textit{2} SLs with \textit{x}=1.2 and 1.6. The total thickness of the SLs was maintained to 200 nm. Fig. 4(a) shows the variation of PL intensity of the SLs as a function of the thickness of the SiO\textit{1.2} and SiO\textit{2} layers. Above the SiO\textit{1.2} layer thickness of 6 nm, the PL intensity remains constant at a weak value, as would be expected for bulk SiO\textit{y} film with \textit{x}=1.2. However, the PL intensity is increased at the averaging zone (>3 nm, shaded area) where the average oxygen content (\textit{y}) corresponds to 1.6; the value at which bulk SiO\textit{x} also displays the maximum PL intensity. In fact, the actual PL intensity between bulk SiO\textit{1.6} and SiO\textit{1.2}/SiO\textit{2} SL with 2 nm thickness were comparable as well. On the other hand, in the case of \textit{x}=1.6, the variation of PL intensity shows a different pattern as shown in Fig. 4(b). The higher PL intensity of SLs with thicker layer thickness abruptly decreases as the layer thickness decreased to the averaging zone where the average oxygen content (\textit{y}) corresponds to 1.8 of bulk SiO\textit{y} films.

4. Conclusion

In conclusion, the oxygen content of the SiO\textit{x} layers in the SiO\textit{x}/SiO\textit{2} SLs grown by IBSD could be successfully determined and controlled with in situ XPS analysis. Although the dependence of the PL intensities on the SiO\textit{x} stoichiometry from bulk SiO\textit{x} films and SiO\textit{x}/SiO\textit{2} SLs seem to differ, the stoichiometry dependence, when scaled for the overall film stoichiometry, was nearly the same. This means that PL property of the SiO\textit{x}/SiO\textit{2} SLs with very thin layers can be described well by the averaged composition of the entire film. Therefore, SL with very thin SiO\textit{x} and SiO\textit{2} layers may be viewed as an effectively homogenous SiO\textit{y} film (\textit{y}>\textit{x}). This result indicates that the PL property of the SiO\textit{x}/SiO\textit{2} SLs is mainly determined by oxygen content.

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