Electroluminescence of as-sputtered silicon-rich SiO\textsubscript{x} films

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A B S T R A C T

Si-rich oxide films (SiO\textsubscript{x}, 0 < x < 2) were synthesized by reactive magnetron sputtering of a single Si target in a gas mixture of argon and oxygen. Intense visible electroluminescence was observed from the as-deposited SiO\textsubscript{x} film. The microstructure of the as-sputtered SiO\textsubscript{x} films was characterized by Raman and X-ray photoelectron spectroscopy techniques. Nanoscale amorphous Si clusters formed in the as-sputtered films. The electroluminescence was attributed to the oxygen-deficient defect luminescent centres and the formation of the amorphous Si nanoclusters.

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1. Introduction

Although it is difficult for bulk silicon to emit visible light at room temperature (RT) (due to silicon's indirect bandgap nature \[1\]), Si nanocrystals (nc-Si) embedded in a transparent dielectric SiO\textsubscript{2} matrix have been demonstrated as robust light emitters and are thus promising for optoelectronic integration devices in Si technology \[2–8\]. The standard approaches of synthesizing nc-Si include ion implantation of silicon into an amorphous SiO\textsubscript{2} matrix \[9\] or deposition of Si sub-stoichiometric oxide films using chemical vapour deposition \[10–12\], sputtering \[13–15\] or, reactive evaporation \[16,17\]. A high temperature (higher than 1050 °C \[10\]) annealing is needed for crystallization of the excess Si into silicon nanocrystals to give rise to nc-Si/a-SiO\textsubscript{2}. Visible electroluminescence (EL) from various nc-Si/a-SiO\textsubscript{2} films has been observed and the luminescence properties have been studied extensively. The origins of the EL are usually ascribed to either the quantum confinement effect of excitations caused by their spatial confinement within the nc-Si [3,5,6,8] or radiative recombination of charge carriers at defect luminescent centres [2,5,18,19]. Luminescence from as-sputtered amorphous SiO\textsubscript{x} films is still unexplored. Although electroluminescence in absence of crystalline nanostructures has been reported at 77 K \[20\], there are few studies that correlated the origins of the emitted light with the presence of its nanostructure. This paper presents the EL studies of the as-sputtered amorphous SiO\textsubscript{x} films synthesized by magnetron sputtering of Si target in oxygen-deficient atmosphere. The chemical and atomic structures of the as-sputtered films are explored in great detail by X-ray photoelectron spectroscopy (XPS) and the Raman technique. The origin of the electroluminescence is explored.

2. Experimental details

A reactive radio frequency (13.6 MHz) magnetron sputtering system (E303A, Penta Vacuum) was employed to deposit SiO\textsubscript{x} films from a Si target (3 inch, 99.999% in purity) in a mixed Ar/O atmosphere at a controlled gas flow rate. The substrates used in this study were p-type Si (100) wafers. In this method, Si concentration can be controlled by varying the Ar/O flow rate ratio. Prior to deposition, the wafers were ultrasonically cleaned consecutively in acetone and ethanol for 20 min each followed by rinse in de-ionized water. The Si target was placed 80 mm above the substrate, and the base pressure of the chamber was lower than 1.3 × 10\textsuperscript{-6} Pa. During deposition, the target power and sputtering pressure were fixed at 200 W and 0.2 Pa, respectively. The variation of the Ar/O\textsubscript{2} flow rate ratio was achieved by varying the oxygen flow rate between 0.8 and 3.0 sccm while maintaining the Ar flow of 40 sccm. In order to remove the possible contaminations, the target was pre-sputtered for 15 min, and the substrates were pre-etched for 15 min before the target shutter was opened to allow commencement of deposition. The resulting SiO\textsubscript{x} films are ∼ 50 nm in thickness with the composition varying from SiO\textsubscript{0.6} to SiO\textsubscript{2}. To fabricate the light-emitting structure, a 1 µm aluminum layer was sputtered on the backside of the sample as the back contact. Indium tin oxide (ITO) of 80 nm in thickness was sputtered on the surface of the sample through a hard shadow mask with pad radius of 0.6 mm. The ITO pad acts as both gate electrode and EL emission window. The composition and chemical states of the films were determined by X-ray Photoelectron Spectroscopy (XPS).
analysis using a Kratos-Axis spectrometer with monochromatic Al Kα (1486.71 eV) on plan-view samples at a normal take off angle. Survey scans and high-resolution spectra were acquired using pass energies of 160 and 40 eV, respectively. Deconvolution of the XPS curves was conducted by using a fitting procedure based on the summation of Gaussian functions after Shirley background subtraction. The crystallinity of the film was characterized using Raman spectroscopy (Renishaw 1000 Ramascope system) with 633-nm line excited by He–Ne laser (The samples used for Raman characterization are ~400 nm in thickness). The EL measurements were carried out with a Dongwoo Optron PDS-1 photomultiplier tube detector together with a Dongwoo Optron DM150i monochromator.

3. Results and discussions

3.1. Electroluminescence response of the as-sputtered films

Intense and visible EL spectra are observed from the as-sputtered SiOₓ films when a negative voltage is applied to the ITO gate. All the samples exhibit similar EL spectra. No EL was detected under a positive gate voltage due to insufficient hole injection from the ITO gate. Fig. 1 shows the EL spectra from a SiO₀.₆ film under various gate voltages. Generally a broad EL spectrum is observed spreading over a visible wavelength range of ~300~900 nm. The EL intensity increases with the applied voltage. Fig. 2 shows EL spectra from as-sputtered SiO₀.₆, SiO₁.₀ and SiO₁.₄ films under a gate voltage of ~–15 V, where the EL intensity increases with Si concentration. Electrical field induced light emissions are usually observed from SiOₓ films after high temperature annealing to induce formation of nc-Si [13–15]. It is exciting to observe light emission from as-deposited (thus amorphous) SiOₓ films in which no nanocrystals are formed yet. The following sections will be devoted to uncover the light emission mechanism in these amorphous SiOₓ films.

3.2. Formation of Si nanoclusters as revealed by Raman spectra

Fig. 3 shows the Raman spectra of the as-deposited SiOₓ films with varied Si concentrations. The Raman spectra of a stoichiometric SiO₂ films is also obtained by the same method for comparison. The sharp peak located at ~520 cm⁻¹ and the weak peak at ~300 cm⁻¹ are due to the phonon modes of the crystalline Si. Since the as-deposited films are amorphous, these crystalline Si peaks originate from the crystalline silicon substrate. For the SiO₂ film, only substrate peaks are observed because the Raman efficiency of amorphous SiO₂ (a-SiO₂) is too low to give rise to detectable Raman signals, unless the a-SiO₂ film is sufficiently thick (thicker than several micrometers). Raman scattering from our as-deposited a-SiO₂ film of 400 nm in thickness is hardly detected. However, in Si-rich films, broad Raman peaks are observed in addition to the substrate peaks, and their features change depending on Si concentration. A slight increase in the Si concentration (SiO₁.₄) results in a broad Raman peak centred at around 160 cm⁻¹. With increasing Si concentration, that peak intensity increases (SiO₁.₀ and SiO₀.₆) and another broad peak at 480 cm⁻¹ also appears and grows (SiO₀.₆). These two broad Raman peaks are
the characteristic peaks for amorphous Si. These Raman features are in good agreement with the results by Kanzawa et al. [21] as well as Nesheva et al. [22]. By comparing their results with the theoretically calculated density of states (DOS) reported by Feldman et al. [23], Kanzawa et al. found their Raman spectra came from Si33 (a Si nanocluster composed of 33 Si atoms) and Si45 (a Si nanocluster composed of 45 Si atoms). Nesheva et al. also noted that SiOx samples annealed at low temperature (250 °C) would have no other features except for Si substrate peaks in the Raman spectrum due to the absence of the amorphous Si phase, whereas for the samples annealed at higher temperature (700 °C), strong Raman bands at 150 and 480 cm⁻¹ appeared due to formation of small Si domains as a result of phase separation. It is shown that a minimum size of amorphous Si domains is required to give rise detectable Raman signals. Besides, it also can be observed that Raman spectra of our as-deposited Si-rich SiOx films exhibit a high-frequency shoulder at around 550 cm⁻¹, extending up to 700 cm⁻¹. This high-frequency shoulder is attributed either to the Si nanoclusters as suggested by Kanzawa et al., or, to the phonon mode of the interface between Si and SiO2 as suggested by Denisov et al. Therefore, it can be concluded that the as-deposited SiOx films are chemically inhomogeneous. During the reactive sputtering, because there is insufficient oxygen to take part in the reaction to form stoichiometric SiO2, some small-size amorphous Si domains (i.e., Si clusters) are bound to form. The strong decrease of the 520 cm⁻¹ band intensity (compared with a pure SiO2 film) supports this suggestion as the absorption of amorphous Si in the blue wavelength region is significantly higher than that of Si oxides.

Since the formation of Si clusters takes place during the deposition, the size of the amorphous Si clusters will be strongly affected by the availability of excess Si (i.e., Si concentration). Here, by comparing with the rescaled calculated DOS spectrum of Si33, and Si45 clusters by Kanzawa et al., we can have a qualitative estimation of the size of the amorphous Si clusters. In the DOS spectrum, both Si33 and Si45 clusters show a low-frequency component at around 160 cm⁻¹ and a high-frequency component at around 480 cm⁻¹. But the spectral features of these two clusters are quite different. For the smaller Si33 cluster, the intensity of the low-frequency component is higher than that of high-frequency component, whereas, with increasing cluster size, for the larger Si45 cluster, the intensity of the low-frequency component becomes slightly lower than that of the high-frequency component. In the SiO0.6 spectrum in Fig. 3, the intensity of the low-frequency peak at 160 cm⁻¹ is comparable with (even slightly higher than) that of the high-frequency peak at 480 cm⁻¹. Therefore, it is reasonable to assume that in SiO0.6 the amorphous Si nanoclusters are of a size comparable to that of Si33. In films of lower Si concentration (SiO1.0 and SiO1.4), the intensity at 160 cm⁻¹ is very weak, and undetectable at 480 cm⁻¹. This indicates that, in these films, the Si clusters are too small (far smaller than Si33) to be detected in Raman. Also note that the amorphous peaks of the as-deposited films are rather broad in Raman spectra, probably due to the wide size distribution of the Si clusters.

3.3. Chemical structure of the as-deposited film

There exist two main models depicting atomic structures in amorphous SiOx films, i.e., the "random bonding model" (RBM) [24] and the "random mixture model" (RMM) [25]. In the random bonding model, the local bonding is considered statistical in nature, and is characterized by five different local bonding possibilities: Si–Si4, Si–Ow, where w = 0, 1, 2, 3, 4. Whereas the random mixture model assumes that nanoscale regions may be dominated by Si–Si or by Si–O bonding [25]. Fig. 4 shows the Si 2p XPS spectrum for the as-deposited SiO0.6, SiO1.0, and SiO1.4 films. The Si 2p core-level spectrum possesses two main peaks, corresponding to the Si–Si4 and Si–SiO4 tetrahedrons. Moreover, the Si 2p lines of both the Si0 and Si4⁺ are not symmetrical, and are separated by a flat region where the intensity does not drop to zero. Therefore, contributions from Si suboxides (Si1⁺, Si2⁺, and Si3⁺) should be considered in order to account for the intensity level of the intermediate region. As the SiOx films were synthesized by reaction of the sputtered Si atoms with oxygen, it is quite possible that the oxidization proceeds with zero, one, two, three, or all four Si–Si bonds being replaced by Si–O bonds. We thus expect five components Si0, Si₁⁺, Si₂⁺, Si₃⁺ and Si₄⁺ in the films. This assumption is comparable to the RBM, and also represents the common chemical features at the Si/SiO2 interface [26]. Based on this assumption, deconvolution of the XPS curves gives rise to 5 peaks, corresponding to Si0, Si₁⁺, Si₂⁺, Si₃⁺ and Si₄⁺ (dotted curves in Fig. 4). The deconvolution procedure is similar to the approach of Hohl et al. [27]. The deconvolution of the XPS curve was conducted by decomposing the Si 2p line into Si 2p3/2 and Si 2p1/2 lines with intensity ratio 1:2 and a fixed spin-orbit splitting of 0.6 eV as an atomic property. Only the sum of the Si 2p1/2 and 2p3/2 partner lines is shown for a clear presentation. The full width at half maximum (2Γ) was assumed to be the same for both lines, but allowed to vary from Si0 to Si4⁺, and the relative weight (W) was allowed to vary without constraint. The Si 2p XPS spectrum was fitted by a superposition of five Gaussian peaks (Si0, Si₁⁺, Si₂⁺, Si₃⁺ and Si₄⁺), corresponding to the situation where no Si–Si bond, one Si–Si bond, two Si–Si bonds, three Si–Si bonds, or all four Si–Si bonds had been replaced by Si–O bonds [27]. The best fitting results was summarized in Table 1. As shown, there are sufficient Si suboxides in the as-deposited films besides the Si and SiO2 species, which shows a chemical feature predicted by RBM. If the Si-rich SiOx is homogeneous in atomic distribution (i.e., RBM), the
probability of the nth tetrahedral configuration can be calculated according to the following equation as \( C_n \) (n = 1 through 5, corresponding to \( \text{Si}^0, \text{Si}^+, \ldots \text{ and } \text{Si}^{4+} \)) as a function of concentration x. [25]:

\[
C_n(x) = \frac{4^n}{(4-n)!} [\frac{1}{2} x^n] \left[ \frac{1}{2} (2 - x) \right]^{4-n} 
\]

(1)

The relative concentration of each chemical state can be calculated by \( C_n(x)/\sum_{n=1}^{5} C_n(x) \). The calculated results for all the five possible states (\( \text{Si}^0, \text{Si}^+, \ldots, \text{ and } \text{Si}^{4+} \)) at x = 0.6, 1.0 and 1.4 are also shown in the RMB column of Table 1. Comparing the numbers in the XPS column and the RBM column, it is obvious that the measured (XPS results) data do not support the random bonding theory (too big a discrepancy). In other words, the atomic distribution of Si in \( \text{SiO}_x \) films is not homogeneous and the \( \text{Si}^0 \) is too high compared with that predicted by RMB. This supports the hypothesis of formation of nanoclusters during sputtering. In addition, XPS results in Table 1 also show an increase in \( \text{Si}^0 \) concentration with increasing Si concentration, in good agreement with the Raman results of Si nanoclusters size increase with increasing Si concentration.

3.4. Formation of Si nanoclusters as revealed by XPS valence band spectra

Fig. 5 shows high-resolution O 2p XPS valence band spectra for as-deposited \( \text{SiO}_{0.6}, \text{SiO}, \text{SiO}_{1.4} \) and a-\( \text{SiO}_2 \) samples. In the valence band of an a-\( \text{SiO}_2 \) film three groups of components can be distinguished. A feature labelled as A located at 6–7 eV, corresponds to the O 2p lone-pair band. Two other components labeled B and C at higher binding energies correspond to a strong interaction of O 2p states with Si 3p and Si 3s level, respectively. In films with excess Si, aside from these three groups, an additional group located at D, 1–2 eV above its valence-band edge, is found. The XPS valence band spectral features of \( \text{SiO}_x \) films show good agreement with the theoretical calculation of silicon’s valence band density of states [28]. The additional group, D, is attributed to be the interaction between Si orbitals which give states at these energies [29]. According to the RBM, the signal of group D cannot be observed when the Si concentration is low (x in \( \text{SiO}_x \) is higher than 1.0) [17]. Calculation also indicates that a minimum length of 10 atoms in the Si–Si chains is required for the Si–Si bonding to be observed in the valence band [28]. In our \( \text{SiO}_{1.0} \) and \( \text{SiO}_{0.6} \) films, a strong Si peak intensity (Group D) is observed and is also noticeable in the spectra in very low Si concentration sample (\( \text{SiO}_{1.4} \)). As such, the valence band spectral features also support the hypothesis of existence of Si–Si long chains (Si clusters) in the films. Again, with increasing Si concentration, the intensity of group D increases, and, at the same time, the group D spectrum slightly broadens. The increased intensity and broadening of the spectral feature imply that the probability that a given Si is surrounded by other Si atoms has increased, so does the probability of interaction between silicon orbitals [17]. These features, although not pronounced, depict an increase in Si nanocluster size with increasing Si concentration. This provides an additional confirmation that the Si nanoclusters form during deposition and the size increases with Si concentration.

3.5. Formation mechanism of Si nanoclusters

The formation of the amorphous Si clusters in the \( \text{SiO}_x \) films is believed to result from the high kinetic energy of the sputtered Si atoms. During sputtering, some of the sputtered Si atoms react with oxygen atoms with either full oxidization to form \( \text{SiO}_2 \) and some partially oxidize to form Si suboxides; on the other hand, certain sputtered Si atoms are not oxidized at all because of the deficient oxygen ambient. These non-oxidized Si can deposit on the substrate directly. The mean free path of the sputtered particles can be estimated from Equation (2) [30]

\[
\lambda_d = \frac{1}{\pi (r_A^2 + r_B^2) n_B} 
\]

(2)

Where, \( r_A \) corresponds to the atomic radius of a sputtered particle and \( r_B \) corresponds to the atomic radius of argon; \( n_B \) is the particle density (\( = N/V = P/kT \)) of Ar in the chamber. \( r_A \) is 0.191 nm, \( r_B \) is 0.110 nm. Note that the chamber pressure was 0.2 Pa and the chamber temperature was 323 K during deposition. Therefore the non-oxidized Si atoms would have a mean free path of 70 nm. At a target-to-substrate distance of 80 mm, this corresponds to a probability that \( \sim 50\% \) sputtered silicon atoms reach the substrate without any collisions [31]. Thus, a significantly high fraction of energetic sputtered silicon particles arrive at the substrate without kinetic energy loss, which enables the silicon atoms to migrate on the growing films surface to form nanosized Si clusters; bombardment of the energetic particles on the growing films surface accelerates this surface migration, also promoting the formation of the Si nanoclusters.

<table>
<thead>
<tr>
<th>Si Species</th>
<th>( \text{SiO}_{0.6} ) (at.%)</th>
<th>( \text{SiO} ) (at.%)</th>
<th>( \text{SiO}_{1.4} ) (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS</td>
<td>RMB</td>
<td>XPS</td>
<td>RMB</td>
</tr>
<tr>
<td>Si-(Si_{2})</td>
<td>30.37</td>
<td>23.38</td>
<td>21.62</td>
</tr>
<tr>
<td>Si-(Si_{3})</td>
<td>24.65</td>
<td>41.67</td>
<td>17.68</td>
</tr>
<tr>
<td>Si-(Si_{4})</td>
<td>18.01</td>
<td>26.35</td>
<td>9.587</td>
</tr>
<tr>
<td>Si-(SiO_{3})</td>
<td>12.08</td>
<td>6.42</td>
<td>18.81</td>
</tr>
<tr>
<td>Si-(SiO_{4})</td>
<td>14.86</td>
<td>0.98</td>
<td>31.28</td>
</tr>
</tbody>
</table>

Table 1: Comparison the relative weights of the different Si chemical states yield by the XPS with that calculated according to RBM.
Fig. 6. Deconvolution of the EL spectrum from as-sputtered SiO_{0.6} into the following EL bands: ~480, ~600, and ~710 nm bands.

3.6. Origins of electroluminescence

From the discussions above, it is therefore clear now that the light emission from the as-sputtered amorphous SiO_{x} film is attributed to the formation of amorphous Si nanoclusters in the film. Since there is a high density of amorphous Si nanoclusters in the gate oxide layer, carrier tunnelling can take place between adjacent nanoclusters [32,33]. A large number of such nanoclusters distributed throughout the oxide can form many conductive tunnelling paths which significantly increase the conductance of the gate oxide. Under negative gate voltage, electrons and holes can be injected from the ITO gate and the p-type Si substrate, respectively. The injected electrons and holes can tunnel through the tunnelling paths formed by the Si nanoclusters, and recombine at the luminescent centres. As the EL property is mainly determined by the numbers of the injected electrons and holes available for the radiative recombination, the key parameter in determining the EL properties will be the current density passing through the device [5,7,8]. The increase in the EL intensity with increasing Si concentration can be interpreted as follows. In samples of higher Si concentration, a higher number of Si nanoclusters are formed, resulting in more tunnelling paths and higher current conduction, which in turn, gives rise to more light emission: with increase in the current conduction, more electrons from the ITO gate and more holes from the p-type Si substrate are injected into the amorphous Si nanostructure, leading to an increase in the radiative recombination of the injected electrons and holes and thus an increase in the EL intensity.

The origin of the light emission was thought to be the quantum confinement effect of the Si clusters, which is thus associated with a size-dependent shift in the light emission energy [3,5,6,8]. However, as shown in Fig. 2, there is no obvious change in the EL position with Si concentration (i.e., size of the nanoclusters). Thus, the quantum confinement effect cannot explain the current results. Instead, an oxygen-deficient defect model, in which oxygen defect functions as a defect luminescent centre, seems to be a more suitable explanation for the current situation. According to this model, EL comes from the recombination of electron–hole pairs on the oxygen-deficient defects in the SiO_{x} films, and various oxygen-related defects may emit photons with energy in a range of 1.9 eV–2.7 eV [2,5,18,19].

The EL spectra can be deconvoluted into three Gaussian-shaped EL bands, as demonstrated in Fig. 6 for the SiO_{0.6} film under a gate voltage of ~15 V, where the main peak locates at ~600 nm (~2.0 eV) and two shoulder bands center at ~480 (~2.7 eV) and ~710 nm (~1.8 eV), respectively. Defects have been proposed as luminescent centres of SiO_{x} films [2,5,18,19], such as the weak-oxygen-bond (WOB, O–O) defect, neutral oxygen vacancy (NOV, O_{3}^{0}=Si–Si=O_{3}^{0}, where = represents bonds to three oxygen atoms), non-bridging oxygen hole center (NBOHC, O_{3}=Si–Si=O_{3}^{0}, where • represents an unpaired hole), D centre and E’ centre. Among these defects, the NOV and NBOHC are most widely observed in magnetron sputtered SiO_{x} films. The NOV [34] and NBOHC [35,36] usually emit photons with energies of 2.7 and 2.0 eV, respectively. From XPS spectra there are high content of Si^{1+}, Si^{2+} and Si^{3+} (Si suboxides) besides elemental Si and Si^{4+}. The presence of Si suboxides in these films is natural because the formation of SiO_{x} is in a purposely oxygen-deficient ambient during reactive magnetron sputtering. Si suboxides contain high density of oxygen-related defects (i.e., the NOV and the NBOHC [19]). Thus the ~480 nm and ~600 nm EL bands are ascribed to the NOV and the NBOHC, respectively. Amorphous Si quantum dots have been reported to generate luminescence bands at ~700 nm due to the quantum confinement effect of electron-hole pairs [37]. Thus the 710 nm band is believed to originate from the carrier radiative recombination in the amorphous Si nanoclusters.

4. Conclusions

Intense visible electroluminescence is observed from as-sputtered oxygen-deficient SiO_{x} films. Raman spectroscopic studies, XPS bonding structure analysis and XPS valence band spectroscopic studies all confirm the existence of Si nanoclusters in the as-sputtered amorphous films. The light emission from amorphous SiO_{x} films is attributed to the nanoscale amorphous Si clusters formed during energetic sputtering. The light emission increases with increasing Si concentration as a result of formation of more channeling paths of chains of Si nanoclusters. The emission of light is believed to come from the Si nanoclusters and the oxygen-deficient defect centres such as the neutral oxygen vacancy (O_{3}^{0}=Si–Si=O_{3}^{0}) and non-bridging oxygen hole centres (O_{3}=Si–Si=O_{3}^{0}).

Reference


