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Electroluminescence from Au/Si oxynitride film/Si structures with the films having different chemical compositions

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Abstract. Si oxynitride films (with thicknesses of about 40–80 Å) with different chemical compositions were deposited on Si wafers by three kinds of method: electron cyclotron resonance (ECR) chemical vapour deposition, magnetron sputtering, and direct nitration of Si wafers in an ECR plasma. The chemical composition of Si oxynitride films was examined by x-ray photoelectron spectroscopy. Electroluminescence (EL) from the semitransparent Au/Si oxynitride film/Si structures, and the effects of chemical composition of the films on EL have been studied. The dependence of EL on thermal annealing has also been reported. Experimental results show that the dominant EL peak position varies from 640 to 700 nm, but the shoulders at about 520 and 820 nm have no apparent shift when the Si content in the Si oxynitride films increases.

1. Introduction

Electroluminescence (EL) from a Au/SiO_2 (500 Å)/Si-rich oxide (200 Å)/n-Si structure was first reported by DiMaria *et al* [1] in 1984. They obtained silicon oxide layers using the chemical vapour deposition (CVD) technique. After annealing at 1000 °C in a N_2 ambient, EL can be observed under forward-bias voltages greater than 15 V. The present authors have reported EL from structures of semitransparent Au/ultra-thin Si-rich SiO_2 film/p-Si with a forward bias greater than 4 V [2]. The Si-rich SiO_2 films were deposited on p-Si using the RF magnetron sputtering method. Compared with the work of DiMaria *et al*, the thicknesses (about 30–80 Å) of the dielectric films in [2] were far thinner, and then the threshold voltages for EL are much lower. Silicon nitride films are usually used in the microelectronics industry because of their excellent insulating properties [3–7], and their potential optoelectronic applications are receiving more and more attention. Boonkosum *et al* [8] have applied a hydrogenated amorphous silicon nitride (a-SiN:H) layer as a luminescent active layer in a light-emitting device with a glass/ITO/p-(a-SiC:H)/i-(a-SiN:H) (250–1000 Å)/n-(a-SiC:H)/Al structure. Deshpande *et al* [9] have reported weak EL from an ITO/a-SiN:H (1000 Å)/Si structure during their extensive studies on the optical

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properties of a-SiN:H films. We have replaced the SiO_2 with Si oxynitride as ultra-thin dielectric films to form semi-transparent Au/ultra-thin silicon oxynitride film/p-Si structures and reported more efficient visible EL from the structures. The silicon oxynitride films were made using the method of RF magnetron sputtering or direct nitration of Si wafers in an electron cyclotron resonance (ECR) plasma [10, 11]. Most recently, Beyer *et al* [12] have prepared Al/silicon oxynitride/Si solar cells and an improved thermal stability was found in comparison with that using a silicon oxide film as a tunnel insulator.

In this paper, we compare EL from Au/ultra-thin Si oxynitride film/Si structures with the films having different chemical compositions and study the thermal annealing effects in a N_2 ambient and in vacuum.

2. Experiments

The substrates used in this experiment were (100)-oriented, 5–9 Ω cm, p-type Si wafers. First, the Si wafers were cleaned carefully, and ohmic contacts on the reverse side were formed by evaporating thin Al films and alloying at 530 °C. Then the native oxide layers on Si wafers were removed thoroughly using a HF solution. After washing with a large amount of de-ionized water and drying in a flux of N_2, the Si wafers were immediately transferred to a reaction chamber for vacuum pumping. Three types of method were used to deposit the Si oxynitride films.

(1) *ECR CVD technique.* Two SiH_4:N_2 flow rate ratios of 7:5 and 7:2 were used. The Si oxynitride films deposited using the former and latter ratios are labelled SON1 and SON2, respectively. The base vacuum was around 2×10^{-4} Pa.

(2) *RF magnetron sputtering technique.* A Si–Si_3N_4 composite target was used. The area ratio of Si to Si_3N_4 in the target was about 6%, and the deposited films are labelled SON3. The base vacuum was around 5×10^{-5} Pa and the deposition was carried out in argon (at about 2 Pa) [10].

(3) *Direct nitration in an ECR plasma.* Only N_2 was used as a reaction gas for nitration of the Si surface in an ECR plasma, and the deposited films are labelled SON4. The base vacuum was around 2×10^{-4} Pa and the nitration process is carried out under N_2 at 10^{-2} Pa [11].

The thicknesses of the Si oxynitride films measured by the ellipsometry were in the range 30–80 Å. Thermal annealing of the films was carried out for 30 min in a N_2 ambient at 300 or 600 °C, or in vacuum at 300 °C. Finally, semitransparent Au films (100–200 Å) were evaporated onto the films to form Au/ultra-thin Si oxynitride film/Si structures. The area of the cells is about 3.14 mm^2.

The EL spectra were measured at room temperature using an HRD 1 spectrometer with 5 Å resolution, and the signal was detected with an S1 cathode photomultiplier tube. The spectra have not been corrected for the spectral response of the system.

3. Results and discussion

The deposited films which were examined by x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) show that, besides N and Si, they also contain O atoms. The typical x-ray photoelectron spectra for SON1, SON2 and SON3 are shown in figure 1, and that for SON4 has been shown in figure 1 of [11]. The chemical compositions of SON1, SON2, SON3 and SON4 were analysed to be $Si_8O_{6.1}N_4$, $Si_{11}O_{7.2}N_4$, $Si_{13}O_{11}N_4$ and $Si_{15}O_{8.4}N_4$, respectively, using XPS. It can be seen that the Si content increases

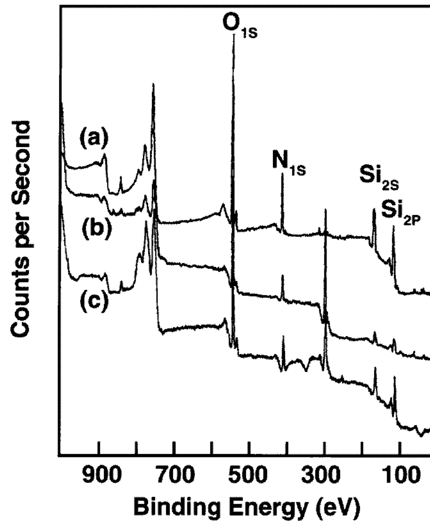

Figure 1. X-ray photoelectron spectra of the Si oxynitride films deposited using the ECR CVD method with a SiH_4:N_2 flow rate ratio of 7:5 (curve (a)), the ECR CVD method with a SiH_4:N_2 flow rate ratio of 7:3 (curve (b)) and the RF magnetron sputtering method with a Si–Si_3N_4 composite target (curve (c)). The measurement step size is 0.400 eV.

monotonically and all four types of film were Si rich in comparison with Si_3N_4. A large amount of oxygen introduced into the deposited films is attributed possibly to the fact that the base vacuum in the deposition system is not high enough, and the thicknesses of the deposited films are ultra-thin.

Under a forward bias of 5 V or greater, EL spectra can be measured from most of the Au/ultra-thin Si oxynitride film/Si structures. The EL spectra of Au/SON1/Si structures are shown in figures 2, curves (a), (b), (c) and (d), for an as-deposited SON1 film, a SON1 film annealed at 300 °C in a N_2 ambient, a SON1 film annealed at 600 °C in a N_2 ambient, and a SON1 film annealed at 300 °C in vacuum, respectively. Two distinct EL bands at around 640 and 520 nm can be seen from the structures with SON1 films as deposited or annealed at 300 or 600 °C in a N_2 ambient. Moreover, for those annealed in N_2, the 640 nm band has a small red shift compared with that in the as-deposited structure, but the 520 nm band has almost no shift. For the film annealed in vacuum at 300 °C, the dominant EL band red shifts to around 660 nm compared with that for the as-deposited structure and the 520 nm band is not detectable. This means that the origins of the 640 and 520 nm bands are not the same.

Figure 3 shows the EL spectra from Au/SON2/Si structures where the SON2 films are as deposited or have been annealed at 300 or 600 °C in a N_2 ambient, or annealed at 300 °C in vacuum. For the structure with the as-deposited SON2 film, the EL spectrum has a dominant peak at around 680 nm accompanied by two weak shoulders at around 820 and 520 nm. With increase in the temperature of annealing in N_2 from 300 to 600 °C, the EL intensity increases and the dominant band has a small red shift. However, on annealing the SON2 film at 300 °C in vacuum, the dominant band blue shifts to around 670 nm compared with that for the as-deposited structure, the shoulder at about 520 nm weakens, and that at about 820 nm is hard to examine.

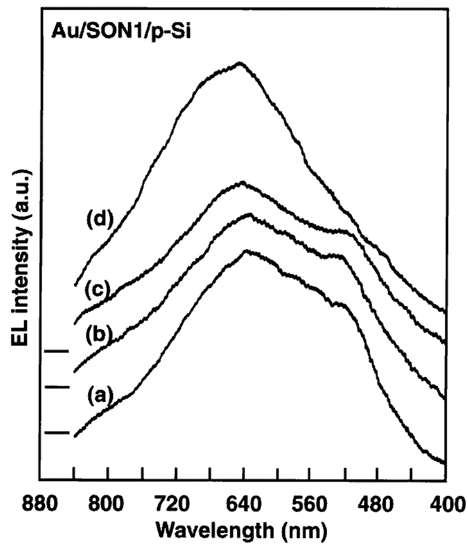

Figure 2. EL spectra of Au/SON1/Si structures under different annealing conditions (a.u., arbitrary units): curve (a), as deposited, forward bias of 10 V, current of 220 mA; curve (b), annealed in N_2 at 300 °C, forward bias of 10 V, current of 350 mA; curve (c), annealed in N_2 at 600 °C, forward bias of 10 V, current of 300 mA; curve (d), annealed in vacuum at 300 °C, forward bias of 10 V, current of 350 mA.

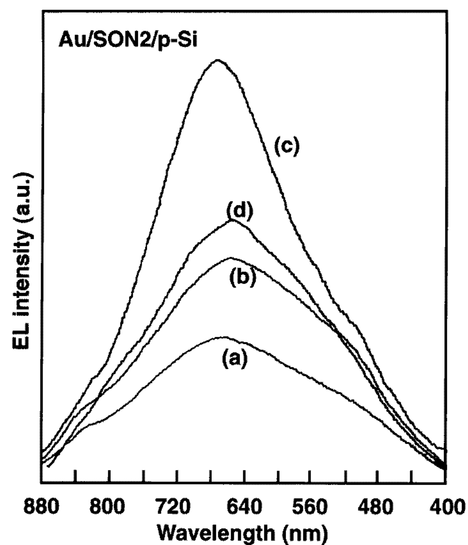

Figure 3. EL spectra of Au/SON2/Si structures under different annealing conditions (a.u., arbitrary units): curve (a), as deposited, forward bias of 7 V, current of 170 mA; curve (b), annealed in N_2 at 300 °C, forward bias of 7 V, current of 100 mA; curve (c), annealed in N_2 at 600 °C, forward bias of 7 V, current of 100 mA; curve (d), annealed in vacuum at 300 °C, forward bias of 7 V, current of 200 mA.

The EL spectra from Au/SON3/Si structures are shown in figure 4 where the SON3 films have been annealed similarly to those of SON1 and SON2. If the SON3 film is not exposed

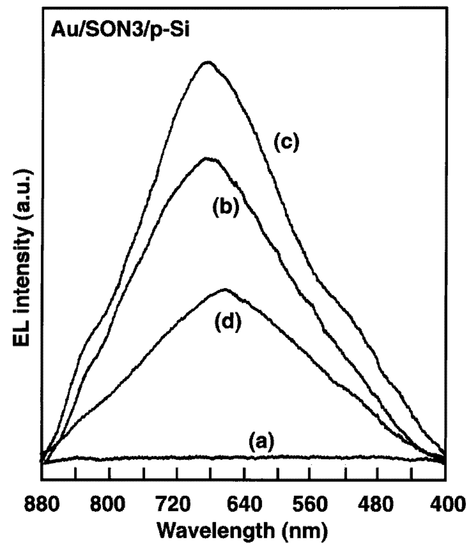

Figure 4. EL spectra of Au/SON3/Si structures under different annealing conditions (a.u., arbitrary units): curve (a), as deposited; curve (b), annealed in N_2 at 300 °C, forward bias of 7 V, current of 70 mA; curve (c), annealed in N_2 at 600 °C, forward bias of 7 V, current of 90 mA; curve (d), annealed in vacuum at 300 °C, forward bias of 7 V, current of 80 mA.

to any thermal annealing, i.e. as deposited, no EL can be observed for the Au/SON3/Si structure. After the SON3 films were annealed in a N_2 ambient at 300 or 600 °C, the EL spectra from the structures have dominant peaks at around 680 nm accompanied by a shoulder at around 820 nm. With increase in temperature of annealing in N_2 from 300 to 600 °C, the EL intensity increases and the peak energy has no evident shift. However, annealing the SON3 film at 300 °C in vacuum, the dominant peak shifts to about 670 nm, and the shoulder at about 820 nm decreases.

The EL spectra from Au/SON4/Si structures with SON4 films annealed at 300 or 600 °C in a N_2 ambient or at 300 °C in vacuum have been reported in our previous letter [11]. It was found that the EL spectra from the structures as deposited or annealed in a N_2 ambient have dominant peaks at around 700 nm, while those annealed in vacuum blue shift to about 680 nm.

The EL behaviour of the four types of structure have common characteristics.

(1) When the Si content in the Si oxynitride films increases from $Si_8O_{6.1}N_4$ to $Si_{15}O_{8.4}N_4$, the dominant EL band red shifts from 640 to 700 nm, which is similar to the photoluminescence (PL) results of Lin and Lee [13]. They have observed that the PL peak wavelengths for a-SiN:H films deposited by plasma-enhanced CVD blue shift when the ratio of NH_3 to $SiH_4 + NH_3$ flow rates increases.

(2) Two shoulders at about 820 and about 520 nm often accompany the dominant EL band, and their peak positions almost do not shift with increasing Si content or annealing in a N_2 ambient or vacuum. Moreover, after annealing in vacuum their intensities decrease apparently and sometimes are even hard to examine.

(3) In comparison with those of as-deposited structures, the dominant EL bands for the structures with SON2 and SON4 films blue shift from 680 and 700 nm to 670 and 680 nm, respectively but, for the structure with a SON1 film, the band red shifts from 640 to 660 nm

when annealed in vacuum. As to the structures with SON3 films, although no EL spectrum has been observed for the structure with an as-deposited SON3 film, after annealing the SON3 film at 300 °C in vacuum the structure shows an EL spectrum with a peak at about 670 nm. These results indicate that the EL peak wavelengths shift towards about 670 nm after vacuum annealing. This is similar to the PL measurement result of porous Si that the PL peak wavelengths focus towards 730 nm after a low-temperature anneal [14]. Because the Si oxynitride films in the present study are ultra-thin, their PL spectra are unable to be measured and studied.

We have considered the effects of reflection and absorption of Au films on the EL spectrum. The absorption coefficient of the Au film increases almost linearly when the wavelength increases from 500 to 1000 nm and the absorption coefficient is about 4 cm^{-1} at 700 nm [15]. Thus the absorption of the Au film (100–200 Å) is too small to lead to any shift in the measured EL spectrum. However, the reflectance of the Au film increases monotonically from about 93% to about 97% when the wavelength increases from 600 to 700 nm and then increases very slowly when the wavelength is greater than 700 nm [15]. Thus, the reflection of the Au film dramatically decreases the EL intensity measured, and the observed EL peak is blue shifted from the actual EL peak. When the measured EL peak wavelength is 670 nm, the actual wavelength should be approximately 690 nm (about 1.8 eV) when reflection is taken into account. However, owing to the reflection of the Au film, all measured EL peaks between 640 and 700 nm have blue shifts compared with actual peaks, and the shifts cannot be used to explain why the EL peak wavelengths shift towards about 670 nm (about 690 nm in fact) after vacuum annealing.

Information about the elemental composition as well as about the chemical bonds of silicon oxide, silicon nitride and silicon oxynitride films has been provided by AES and XPS measurements [16–19]. The structure of β-Si_3N_4 belongs to the hexagonal crystal system and can be described as triply twinned hexagonal close packed (space group, $P6_3/m$), and the structure of α-Si_3N_4 is only a small distortion of the β form [20]. Compared with that for silicon nitride, in the silicon oxynitride, some N atoms are replaced by O atoms, the charge transfer from Si to N is reduced, weakening the remaining Si–N bonds.

Three distinct PL bands from amorphous silicon nitride films at energies of 1.7–2.0 2.4–2.6 and 2.9–3.1 eV have been reported in a number of papers [9, 21–24]. In this paper, the dominant EL band at 640–700 nm (about 1.9–1.7 eV) and the shoulder at 520 nm (about 2.4 eV) are close to the first and second PL bands. Robertson [21] has defined defects in Si nitride to be of four types, namely Si–Si and N–N bonds, and Si and N dangling bonds. He has calculated the Si–Si bond to form a σ state near the valence bond and an empty σ^* state close to the conduction band. He has proposed a model based on the Si–Si (σ–σ^*) bonds separated by 4.6 eV, representing the band edges, and additional electron and hole traps within the gap. All the three bands can be explained by the defect model. The 1.7–2.0 eV band is assigned to radiative recombination between an electron and a hole in the traps (between the N_4^+ and N_2^0 levels), and it was considered as the major mode of recombination in silicon-rich films. The 2.4–2.6 eV band arises from the radiative recombination at the silicon dangling-bond centre, and the 2.9–3.1 eV band is due to recombination either from the conduction band to the N_2^0 level or from the valence band to the N_4^+ level. The broad features observed in our EL spectra can be attributed to the fact that the optical band gaps depend on the film composition and the silicon oxynitride films are amorphous and, as a result, the energy levels of defects are not very well defined and have a distribution.

In our previous studies, we have found that the EL peak positions for the Au/ultra-thin Si oxynitride/Si structures do not vary with increasing bias until the EL structure breaks down, although the junction temperature continuously increases [10, 11], and electron beam

irradiation can induce a new EL band [10]. Moreover, the present EL peak positions are close to the PL peak positions which have been attributed to recombination via defects. For these reasons, we consider that the EL mechanism of Au/ultra-thin Si oxynitride/Si structures are similar to that of Au/ultra-thin Si oxide/Si structure [2]. For both structures, the EL originates from luminescence centres (LCs), i.e. defects or impurities, rather than from the nanosized Si particles in the insulator films. The electrons from the metal and the nanometre silicon particles embedded in the dielectric film, and the holes from the nanometre silicon particles and the Si substrate, respectively, tunnel into the dielectric layers and radiatively recombine via the LCs (defects or impurities) there, while the electron and hole energy levels in nanometre silicon particles increase owing to the quantum confinement effect and thus have an effect on the EL. We refer to this model as the quantum confinement-tunnelling-LC model.

On the basis of this model, we can explain the present experimental results as follows. From the fact that the approximately 520 nm and approximately 820 nm EL shoulders weaken or annihilate after annealing in vacuum or N_2, we suppose that only one type of LC is dominant in the light emission and its density decreases after annealing; thus the intensity can be changed but the peak position does not shift. From the shift of the dominant EL band with increasing Si content or with vacuum annealing, we suppose that there are several types of LC with emission wavelengths in a range 640–700 nm and, with increasing Si content, the densities of the LCs with longer emission wavelengths increase relatively and as a result the EL bands red shift. When annealing in vacuum, the density of the LC with a light emission wavelength of around 670 nm increases relatively and the LC becomes the dominant compared with the other LCs. Thus EL peaks have a tendency to shift towards about 670 nm after annealing in vacuum.

4. Conclusion

In summary, EL from semitransparent Au/Si oxynitride film/Si structures with the films having different chemical compositions have been studied. On increasing the Si content in the Si oxynitride films, the dominant EL bands vary from 640 to 700 nm, while the EL shoulders at around 520 and 820 nm do not shift. The experimental results can be explained as follows; the electrons from the metal and the nanometre silicon particles embedded in the Si oxynitride film, and the holes from the nanometre silicon particles and the Si substrate, respectively, tunnel into the dielectric layers and radiatively recombine via the LCs (defects or impurities) there; only one type of LC dominates the 520 or 820 nm EL band, but several types of LC are responsible for the dominant EL band, and the Si content in the Si oxynitride film or annealing in vacuum can affect their relative contributions.

Acknowledgments

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