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Room-temperature blue luminescence of thermally oxidized $Si_{1-x-y}Ge_xC_y$ thin films on Si (100) substrates

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We measured at room temperature the photoluminescence spectra of the thermally oxidized $Si_{1-x-y}Ge_xC_y$ thin films which were grown on silicon substrates by plasma-enhanced chemical vapor deposition and then wet oxidized at 1100 °C for 20 min. The photoluminescence band with a peak at ~393 nm under the exciting radiation of $\lambda = 241$ nm was observed. Possible mechanism of this photoluminescence is discussed. © *1999 American Institute of Physics.* [S0003-6951(99)01147-X]

During the last few years, special interest has been devoted to the blue-green luminescence of silicon-based materials because they have potential for becoming novel and future photoelectric devices. Among them, silicon-based materials with nanostructures, such as porous silicon,[1] oxidized silicon, and germanium nanocrystallites,[2–5] oxidized SiC nanocrystallites,[6] and so on, are perhaps under the most wide and complete investigations. However, another important type of silicon-based material luminescence, luminescence related to oxygen-deficient defects in amorphous SiO_2 films[7–9] and $Si(1-x)Ge(x)O_2$ films,[10,11] has been paid more and more attention recently. Starting from Mitchell and Page's work,[9] many other groups have worked in this field. Skuja[8] proposed that the well-known optical absorption band at 5.03 eV and the luminescence band at 4.3 eV in amorphous SiO_2 are due to singlet-to-singlet transitions, while the luminescence band at 2.65 eV due to triplet-to-singlet transitions in a silicon-related intrinsic defect, twofold coordinated silicon Si_2^0. A characteristic photoluminescence (PL) band at 3.1 eV in oxygen deficient SiO_2:GeO_2 was also observed.[10,12] In 1995 Ginzburg *et al.* proposed a physics model based on the energy level arrangement of $Si_2^0(Ge_2^0)$ to explain some features of the blue luminescence in amorphous $Si(1-x)Ge(x)O_2$.[11] In addition, even for the cases of the luminescence in the nanostructure materials, the oxygen deficient luminescent centers are often taken into consideration.[13]

Recently, the studies on $Si_{1-x-y}Ge_xC_y$ alloys have been paid great attention because of the considerably greater flexibility, compared to that available in the $Si_{1-x}Ge_x$/Si material system, to control strain and electronic properties in group IV heterostructure materials. Substantial improvements in the growth and characterizing of $Si_{1-x-y}Ge_xC_y$ alloys have already been achieved.[14]

In this letter, we report the photoluminescence spectra from the thermally oxidized $Si_{1-x-y}Ge_xC_y$ thin films on Si (100) showing a photoluminescence band with a peak at ~393 nm under the exciting radiation of $\lambda = 241$ nm. Furthermore, we discuss the possible mechanism of the PL from the oxidized $Si_{1-x-y}Ge_xC_y$ thin films.

The $Si_{1-x-y}Ge_xC_y$ samples used in this work were grown on Si (100) substrates by plasma-enhanced chemical vapor deposition (PECVD).[15] The $Si_{1-x-y}Ge_xC_y$ layers with the thickness of 170 nm were deposited at 600 °C from silane, germane, and ethylene in a hydrogen carrier. After growth, the samples were wet oxidized at 1100 °C for 20 min. In order to clarify the photoluminescence of the oxidized $Si_{1-x-y}Ge_xC_y$ thin films, two different references were used. One was the as-grown $Si_{1-x-y}Ge_xC_y$ sample grown under the same conditions and not experiencing wet oxidation process; the other was a cleaned silicon sample cut from the identical silicon wafer and wet oxidized under the same condition as that of the oxidized $Si_{1-x-y}Ge_xC_y$ samples.

The composition of the $Si_{1-x-y}Ge_xC_y$ thin films before wet oxidation was determined using Auger electron spectroscopy (AES). The fraction of Si, Ge, and C in the films is about 0.16, 0.70, and 0.14, respectively. X-ray diffraction (XRD) result shows that the thin films are polycrystalline.

The oxidized $Si_{1-x-y}Ge_xC_y$ thin films are amorphous according to the result of XRD. The chemical state and the composition of the oxidized $Si_{1-x-y}Ge_xC_y$ films were determined by x-ray photoelectron spectroscopy (XPS). XPS on the $Si_{1-x-y}Ge_xC_y$ samples was also measured for comparison with oxidized $Si_{1-x-y}Ge_xC_y$ films (see Fig. 1). Figure 1 shows that for as-grown and oxidized $Si_{1-x-y}Ge_xC_y$ films, the Si_{2p} peak is at 99.0 (attributed to Si in $Si_{1-x-y}Ge_xC_y$[16]) and 103.0 eV (characteristic of SiO_2[17]), respectively, and the Ge_{3d} peak is at 29.0 (Ge in $Si_{1-x-y}Ge_xC_y$[17]) and 32.6 eV (Ge in GeO_2[17]), respectively. The C_{1s} peak is at 284.6 eV (C–C bonding[17]) for both as-grown and oxidized films. The binding energy of O_{1s} for the oxidized films is 532.7 eV, attributed to O in the mixture of SiO_2 and GeO_2, which is reasonable because 532.7 eV is a little less than the standard data for O_{1s} in SiO_2 533.0 eV.[17] XPS results show that the oxidized film is mainly the mixture of SiO_2 and GeO_2, which can be represented by $Si(1-x)Ge(x)O_2$ for convenience. The ratio of the quantity of Si and Ge in the oxidized $Si_{1-x-y}Ge_xC_y$ films calculated from XPS, Si:Ge, is approximately 1:0.3.

The photoluminescence spectra of the samples were

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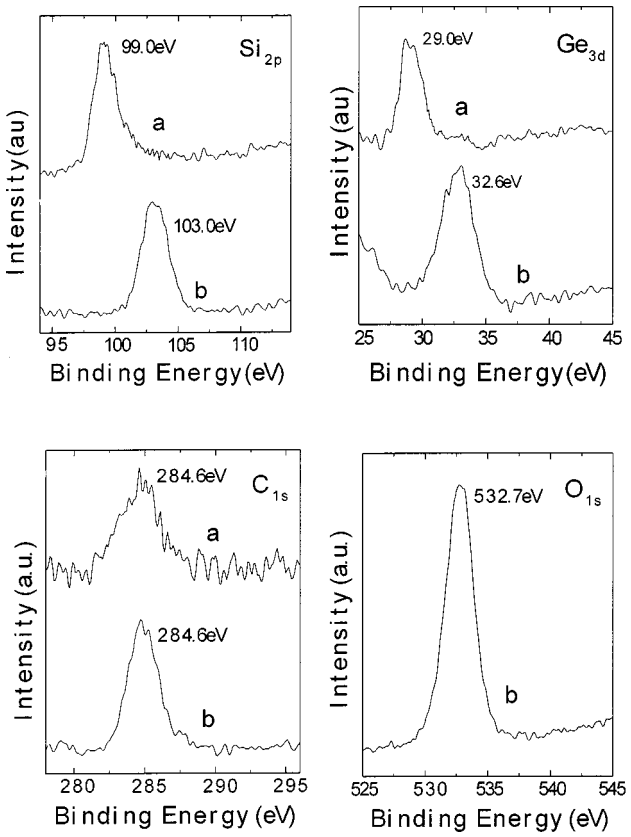

FIG. 1. XPS spectra in the Si_{2p}, Ge_{3d}, C_{1s}, and O_{1s} region from the as-grown and the oxidized $Si_{1-x-y}Ge_xC_y$ thin films on Si (100). (a) The as-grown $Si_{1-x-y}Ge_xC_y$ thin films. (b) The oxidized $Si_{1-x-y}Ge_xC_y$ thin films.

measured by an EG&G Fluoro Max-2 spectrophotometer at room temperature (300 K) and a Xe lamp was used for a light source. Figure 2 shows the PL spectrum from the oxidized $Si_{1-x-y}Ge_xC_y$ sample under the excitation of $\lambda = 241$ nm. A luminescence band with a peak at about 393 nm (about 3.15 eV) was observed. The PL spectra of the two reference samples, the as-grown $Si_{1-x-y}Ge_xC_y$ sample and the oxidized Si sample, were also measured, but neither of

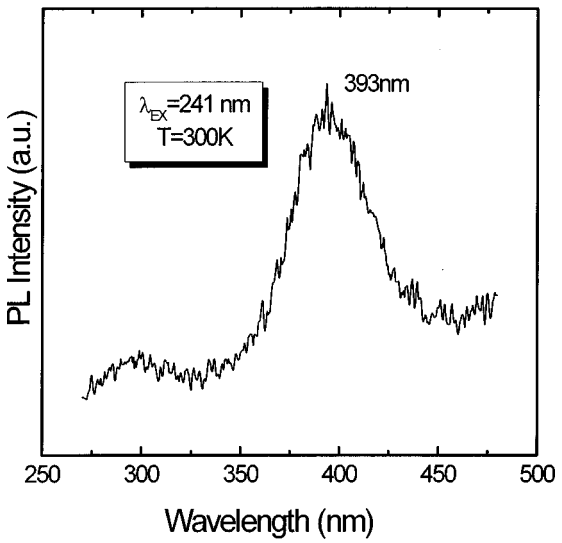

FIG. 2. Photoluminescence spectrum for the wet oxidized $Si_{1-x-y}Ge_xC_y$ thin film on Si (100).

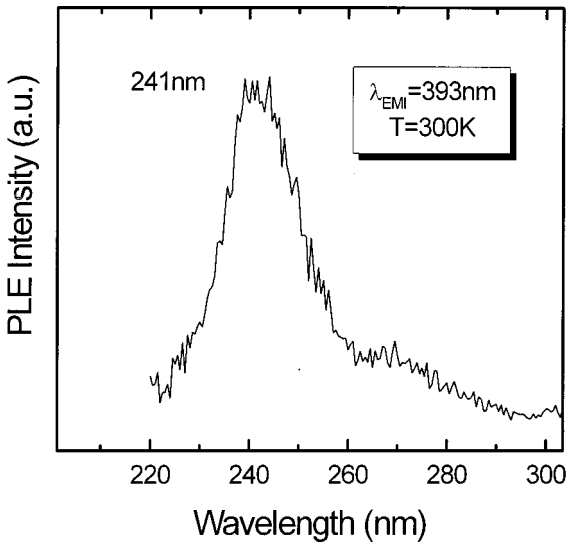

FIG. 3. Photoluminescence excitation spectrum for the wet oxidized $Si_{1-x-y}Ge_xC_y$ on Si (100).

them has photoluminescence under the same measurement condition. In order to study the source of the luminescence from the oxidized $Si_{1-x-y}Ge_xC_y$ sample, we measured room-temperature photoluminescence excitation (PLE) spectrum of the oxidized $Si_{1-x-y}Ge_xC_y$ sample (see Fig. 3). The excitation peak is around 241 nm (about 5.14 eV).

According to the work of Skuja *et al.*,[10] the source of the blue luminescence in oxygen-deficient amorphous $Si(1-x)Ge(x)O_2$ is the twofold-coordinated silicon O–Si–O (Si_2^0) or O–Ge–O (Ge_2^0). The $Si_2^0(Ge_2^0)$ defects contain two nonbonding electrons which form a ground state singlet level (S_0), an excited singlet level (S_1), and a triple level (T_1). The blue luminescence ($\sim$3.1 eV) is attributed to the $T_1 \rightarrow S_0$ transition[10] and it is excited in the region of the Ge-related optical absorption band peaking at 5.14 eV (attributed to the $S_0 \rightarrow S_1$ transition).[10] From the data of XPS and XRD, we can reasonably consider the oxidized $Si_{1-x-y}Ge_xC_y$ film as oxygen-deficient amorphous $Si(1-x)Ge(x)O_2$ film ($x_{EXP} \sim 23\%$ from XPS), among which there is still a little amount of C left from the thermal oxidation process. The excitation peak at 5.14 eV in Fig. 3 is consistent to the $S_0 \rightarrow S_1$ transition of $Si_2^0(Ge_2^0)$, and the luminescence peak at 3.15 eV in Fig. 2 is consistent to the $T_1 \rightarrow S_0$ transition of $Si_2^0(Ge_2^0)$. So the observed luminescence band peaking at about 393 nm from the oxidized $Si_{1-x-y}Ge_xC_y$ sample in Fig. 2 should arise from the twofold-coordinated silicon O–Si–O (Si_2^0) or O–Ge–O (Ge_2^0).

We can explain the mechanism of the photoluminescence from the oxidized $Si_{1-x-y}Ge_xC_y$ sample in terms of the dipole model[11] proposed by Ginzburg *et al.* According to this model, we gave the energy level scheme of the Si_2^0 defects in the oxidized $Si_{1-x-y}Ge_xC_y$ thin films on Si(100) substrates (see Fig. 4). The photoexcited electrons, when delocalized and thermalized, disintegrated into two subsystems: the mobile electrons with energy $E > E_C$ (E_C is the Mott mobility edge), which are responsible for the radiative recombination, and a system of localized electrons with energy $E < E_C$, which setup a system of randomly distributed dipoles. Suffering scattering from randomly distributed dipoles, the mobile electrons lose some energy Δ before recombination,

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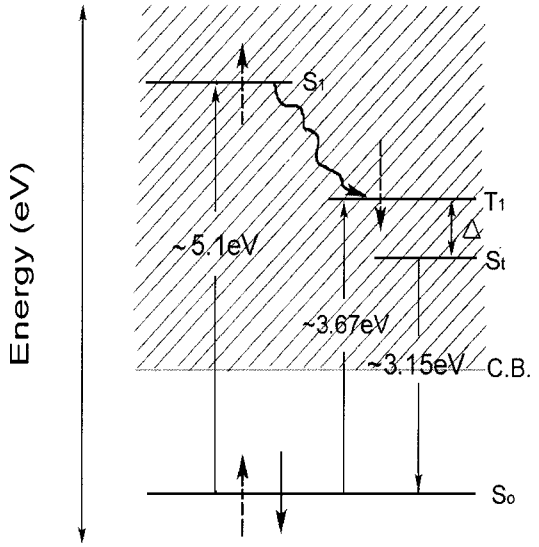

FIG. 4. An energy level scheme of the Si_2^0 defect in the oxidized $Si_{1-x-y}Ge_xC_y$ thin film on Si (100).

where Δ depends on Ge concentration. From the formula $E=3.671-0.74(1-x)^2$ proposed by Ginzburg *et al.*,[11] where $E=3.15$ eV from the result of PL measurement, we can estimate the value of x in the oxygen-deficient amorphous $Si(1-x)Ge(x)O_2$ film as $x_{TH}\sim 16\%$. Taking into account the error arising from the measurement of XPS, the theoretic data is fairly consistent to the experimental data 23%.

The behavior of C during the wet oxidation process of the thin films is very important to the formation of oxygen-deficient amorphous $Si(1-x)Ge(x)O_2$ film. Just after growth and before wet oxidation, some C atoms are substitutional incorporated and make bonds with Si or Ge atoms. When the sample is wet oxidized at 1100 °C, most C atoms depart from the thin film perhaps in the form of CO or CO_2, leaving some nonbonding electrons in $Si_2^0(Ge_2^0)$. So, the substitutional C atoms can improve the formation of the oxygen deficient defects.

In summary, the $Si_{1-x-y}Ge_xC_y$ thin films were grown on Si (100) by PECVD and wet oxidized at 1100 °C for 20 min. The photoluminescence spectra of the thermally oxidized $Si_{1-x-y}Ge_xC_y$ thin films measured at room temperature show a photoluminescence band with a peak at ~393 nm under the exciting radiation of $\lambda=241$ nm. The photoluminescence is related to the twofold-coordinated silicon O–Si–O (Si_2^0) or O–Ge–O (Ge_2^0) defects. The C atoms in the films improve the formation of such defects during the wet oxidation process.

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