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Enhancement in the efficiency of light emission from silicon by a thin Al_2O_3 surface-passivating layer grown by atomic layer deposition at low temperature

M. J. Chen,[a] Y. T. Shih, M. K. Wu, and F. Y. Tsai
Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 106, Republic of China

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Thin Al_2O_3 surface-passivating layers grown by atomic layer deposition at 100 °C were demonstrated to be instrumental in producing efficient light emission from silicon. External quantum efficiency up to 1.3×10^{-4} was observed from silicon metal-insulator-semiconductor light-emitting diodes with a 5 nm Al_2O_3 surface-passivating layer as the insulator, which is more than tenfold that from similar devices with a 5 nm SiO_2 insulator layer thermally oxidized at 1000 °C. Anomalous temperature dependences of the photoluminescence intensities and spectra at low temperatures indicate the presence of bound excitonic traps at the Al_2O_3/Si interface. The enhanced light emission may be attributed to the temporary capture of excitons by the interfacial bound excitonic traps, which effectively reduces nonradiative recombination. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2464190]

Since silicon is the most important material for ultra-large-scale-integration (ULSI) circuits, the monolithic integration of microelectronics and optoelectronics in a single silicon chip has gathered considerable attentions in recent years.[1–17] Few silicon-based light-emitting sources, however, have been able to realize practical applications on optoelectronics. In bulk silicon, where radiative recombination of carriers is a phonon-assisted process due to the indirect band gap, nonradiative recombination proceeds much faster than radiative recombination, causing most carriers to recombine nonradiatively. This leads to a very low quantum efficiency of light emission from bulk silicon ($\eta \sim 10^{-6}$). Therefore, reducing nonradiative recombination of carriers is deemed a promising approach to increase the light-emission efficiency from silicon.

In order to achieve silicon-based light-emitting devices with high luminescence efficiency, nonradiative recombination of carriers has to be reduced to a very low level, both in the bulk and at the surface. Nonradiatve recombination in the bulk can be minimized by using high-quality silicon substrates, such as those grown by the float-zone (FZ) or magnetically confined Czochralski (MCZ) process.[15] Nonradiative recombination at the surface can be suppressed by passivating the surface. The silicon surfaces are conventionally passivated by thermally oxidized SiO_2.[15] The high processing temperatures (usually >700 °C) required to form thermal SiO_2, however, prohibits thermal SiO_2 from applications requiring low-temperature processing. Another way to grow high-quality passivation layers on silicon surface is to use atomic layer deposition (ALD).[18,19] ALD is a surface-controlled layer-by-layer process for depositing thin films with atomic-layer accuracy. During a typical ALD process, an excess of each precursor is alternatively supplied to saturate the surface sites, resulting in self-limiting film growth. Owing to its self-limiting characteristics, ALD offers many advantages, including accurate and facile thickness control, excellent conformality, abrupt interfaces, high uniformity over a large area, good reproducibility, dense and pinhole-free structures, and low deposition temperatures, etc.[18,19] The high quality of ALD films is manifested by the prominence of ALD high-K dielectrics, such as Al_2O_3 and HfO_2, which are poised to replace SiO_2 in the future-generation silicon ULSI circuits.[20] In this study we used ALD to grow thin Al_2O_3 films as the insulator layer in metal-insulator-semiconductor (MIS) light-emitting diodes (LEDs) on silicon at a low temperature of 100 °C. The ALD Al_2O_3 insulator serves as a surface-passivating layer to reduce nonradiative recombination of carriers at the silicon surface, thereby enhancing the light-emission efficiency from silicon.

The ALD Al_2O_3 film was deposited on the silicon substrate held at 100 °C using alternating pulses of $Al(CH_3)_3$ (trimethylaluminum (TMA), the Al precursor) and H_2O (the oxygen precursor) in a N_2 carrier gas flow. The deposited thickness was 5 nm. *n*-type (100) silicon substrates with resistivity of $0.1-1\ \Omega$ cm and grown by FZ method were used in this study. Prior to ALD, the silicon substrates were cleaned in a dilute HF solution to remove the native oxide. The ALD process consisted of a number of identical cycles, each of which contained the following sequence: TMA, $0.1\ s \rightarrow N_2$ purge, $5\ s \rightarrow H_2O$, $0.1\ s \rightarrow N_2$ purge, 5 s. Each ALD cycle deposited ~ 1 Å of Al_2O_3. The thickness of the deposited Al_2O_3 film was controlled by the number of ALD cycles. The gate electrodes of MIS LEDs were prepared by thermally evaporating aluminum on the Al_2O_3-deposited silicon substrates. The aluminum gate electrodes were circular, each with an area of 1.78×10^{-2} cm^2. Aluminum was also deposited on the backside of the silicon substrates as another electrode of the MIS LEDs. To investigate the light-emission efficiency from silicon with different surface-passivating layers, we also fabricated the MIS LEDs with the gate dielectric

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[a] Electronic mail: mjchen@ntu.edu.tw

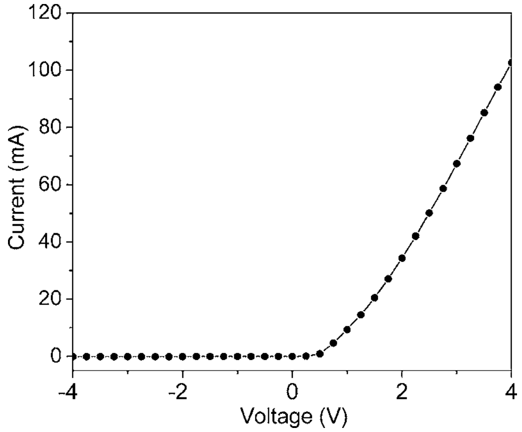

FIG. 1. *I-V* curve of the silicon MIS LED with a 5 nm Al_2O_3 layer as the gate dielectric.

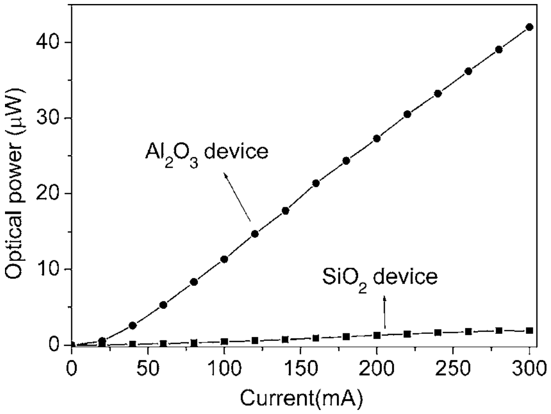

FIG. 3. Room-temperature *L-I* curves of the silicon MIS LEDs with ALD Al_2O_3 or thermal SiO_2 as the gate dielectric.

replaced by a 5 nm SiO_2 layer grown by thermal oxidation at 1000 °C on the same type of silicon substrate.

The 5 nm Al_2O_3 or SiO_2 films in the MIS LEDs were thin enough to allow significant amount of carriers to tunnel through. Figure 1 shows the current versus voltage (*I-V*) curve of the MIS LED with Al_2O_3 as the gate dielectric, which shows a rectifying characteristic. The electroluminescence (EL) spectrum at room temperature is shown in Fig. 2. Under a positive gate voltage, an accumulation layer of majority electrons is formed near the Al_2O_3/Si interface. The electrons tunnel from the silicon to the gate electrode, while the holes tunnel in the opposite direction. After relaxing to the valence band edge, the holes may radiatively recombine with the accumulated electrons to emit light from the Al_2O_3/Si interface. The spectral position of the EL signal around 1.07 eV indicates that the light emission resulted from the transverse optical (TO) phonon-assisted interband transition in silicon.[21]

Figure 3 shows the room-temperature optical power versus injection current (*L-I*) curves of the MIS LEDs with Al_2O_3 or SiO_2 as the gate dielectric. We used an InGaAs *p-i-n* diode placed near the aluminum gate electrode to detect the optical power of the emitted light. The external quantum efficiency for the Al_2O_3 devices was measured to be 1.3×10^{-4}. Since the luminescence was almost blocked by the aluminum gate electrode, only the light emission from the periphery of the device was measured. The internal quantum efficiency was, hence, estimated to be on the order of 10^{-3}. The external quantum efficiency for the SiO_2 devices, on the other hand, was only 5.8×10^{-6}. The EL efficiency of the Al_2O_3 devices was more than one order of magnitude higher than that of the SiO_2 devices. This indicates that, compared to the thermal SiO_2 films grown at 1000 °C, the ALD Al_2O_3 films grown at a temperature as low as 100 °C were more effective in passivating the silicon surface and reducing nonradiative recombination.

The difference in the carrier recombination mechanisms between Al_2O_3- and SiO_2-passivated silicon surfaces were investigated by measuring the temperature dependence of photoluminescence (PL) from these surfaces. Figure 4 shows the PL intensities as a function of temperature for both types of samples. Note that these samples had no metal gate electrodes. With the SiO_2 sample, the PL intensity decreased rapidly when the temperature rose from 10 to 300 K, as a result of thermal activation of nonradiative recombination. The PL intensity of the Al_2O_3 sample, on the contrary, increased as the temperature rose from 10 to 110 K, and then decreased slowly with increasing temperature above 110 K. The PL intensity of the Al_2O_3 sample was greater than that of the SiO_2 sample at temperatures above 60 K. This anoma-

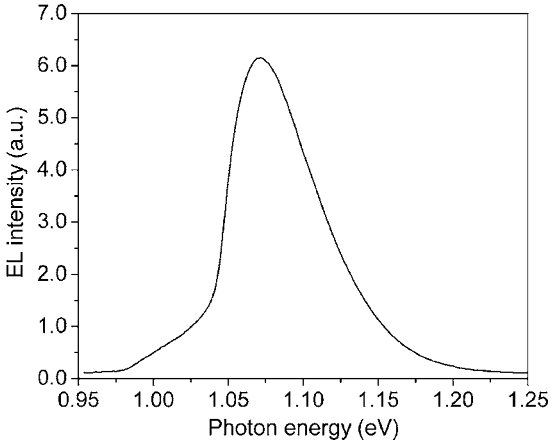

FIG. 2. Room-temperature EL spectrum of the silicon MIS LED with a 5 nm Al_2O_3 layer as the gate dielectric.

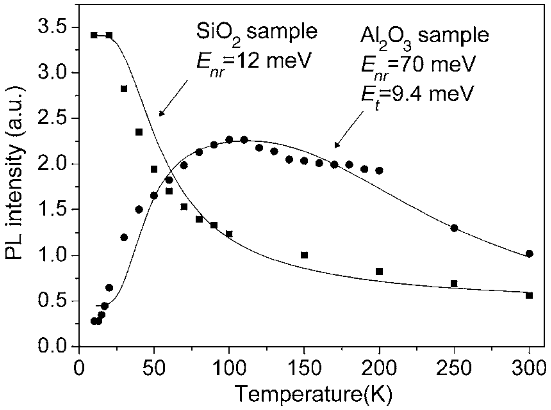

FIG. 4. Temperature dependence of the PL intensity for the silicon substrates with an ALD Al_2O_3 or thermal SiO_2 surface-passivating layer.

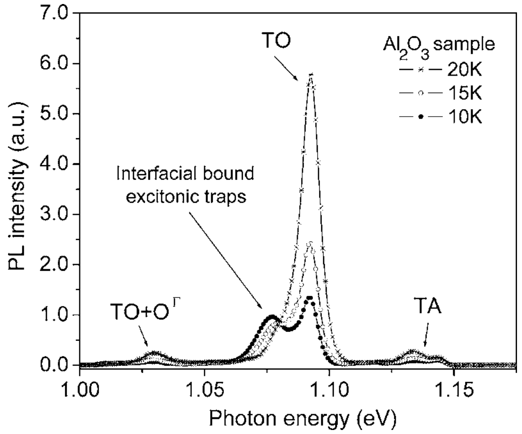

FIG. 5. PL spectra of the silicon substrate with an Al_2O_3 surface-passivating layer at 10, 15, and 20 K.

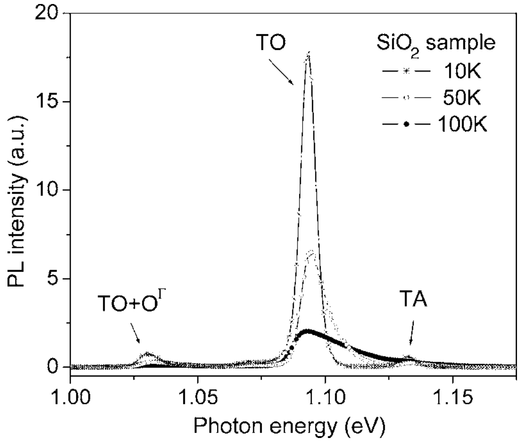

FIG. 6. PL spectra of the silicon substrate with a SiO_2 surface-passivating layer at 10, 50, and 100 K.

lous temperature dependence of PL intensity may be attributed to the bound excitonic traps at the Al_2O_3/Si interface.[16,17,21]

Figure 5 shows the PL spectra of the Al_2O_3 sample at 10, 15, and 20 K, respectively. The PL spectra of the SiO_2 sample at 10, 50, and 100 K are also shown in Fig. 6 for comparison. The PL spectra of both samples contain three peaks, corresponding to the two-phonon ($TO+O^{\Gamma}$), TO, and transverse acoustic (TA) phonon-assisted transitions, respectively.[21] The spectra of the Al_2O_3 sample, however, show an additional peak at energy lower than the main TO peak. This spectral peak may be attributed to the interfacial bound excitonic traps at the Al_2O_3/Si interface. As the temperature increases from 10 to 20 K, this spectral peak gradually diminishes, while the main TO peak significantly intensifies. The intensity of the main TO spectral peak continues to increase with temperature up to 110 K. On the contrary, the TO spectral peak of the SiO_2 sample decreases rapidly with increasing temperature, as shown in Fig. 6. Considering that no spectral signal corresponding to bound excitonic traps appeared in the PL spectrum of the SiO_2 sample at 10 K, the anomalous increase in the main TO spectral peak with temperature, as shown in Fig. 5, may be associated with the decrease of the spectral signal from the interfacial bound excitonic traps in the Al_2O_3 sample.

The anomalous temperature dependence of PL intensity of the Al_2O_3 sample may be explained as follows. At low temperatures, excitons were bound in the traps at the Al_2O_3/Si interface. When the temperature increased from 10 to 110 K, the excitons were thermally ionized to escape from the traps, raising the concentration of free excitons, which in turn increased the PL intensity. In other words, our observed increase in PL intensity with temperature may have been caused by thermal dissociation of bound excitons. At temperatures above 110 K, the PL intensity dropped, as nonradiative recombination became increasingly activated. The activation energies of the nonradiative recombination states and of the dissociation of bound excitons to free excitons, E_{nr} and E_t, respectively, were obtained by fitting the experimental data using the following expression:[21,22]

$$I(T) = \frac{I_0}{[1 + gT^{3/2}\exp(-E_{nr}/k_BT)][1 + c/[1 + bT^{3/2}\exp(-E_t/k_BT)]]}, \quad (1)$$

where I is the PL intensity, T is the temperature, I_0 is the PL intensity at low temperature, k_B is the Boltzmann constant, and g, c, and b are parameters independent of temperature. An efficient nonradiative recombination process has a small value of activation energy, E_{nr}. The solid lines in Fig. 4 are the fitted curves using expression (1). For the Al_2O_3 sample, the activation energy of the dissociation of bound excitons to free excitons, E_t, was calculated to be 9.4 meV, which agrees with the thermal energy at the temperature, 110 K, at which the PL intensity in Fig. 4 showed the maximum. E_{nr} of the Al_2O_3 sample (70 meV) is much larger than that of the SiO_2 sample (12 meV), indicating that the nonradiative recombination states were less thermally active and less efficient for the Al_2O_3 sample. The bound excitonic traps at the Al_2O_3/Si interface captured the excitons and effectively prevented them from decaying quickly through the nonradiative recombination states, and thus were responsible for the higher light-emission efficiency at room temperature.

In summary, light emission from silicon with a thin Al_2O_3 surface-passivating layer deposited by ALD at a temperature as low as 100 °C was studied. The room-temperature EL with external quantum efficiency up to 1.3×10^{-4} was demonstrated for silicon MIS LEDs with an ALD Al_2O_3 layer as the gate dielectric, which is more than tenfold that from similar devices with a SiO_2 insulator layer thermally oxidized at 1000 °C. The low-temperature PL spectra of the Al_2O_3-passivated sample contain a peak that may be assigned to bound excitonic traps at the Al_2O_3/Si interface. The dissociation of bound excitons to free excitons may have been responsible for the observed anomalous temperature dependence of PL intensity. The enhanced light emission from the Al_2O_3-passivated silicon MIS LEDs was attributed to the temporary capture of the excitons by the interfacial bound excitonic traps, which effectively suppressed nonradiative recombination. Our results show that the Al_2O_3 films grown by ALD at low temperature served as good surface passivation layers for silicon LEDs. The low deposition temperatures required for ALD will be useful in the surface passivation of thermally fragile substrates and nanostructures.

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