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Light emission from Al/HfO_2/silicon diodes

T. C. Chen and W. Z. Lai
Department of Electrical Engineering and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

C. Y. Liang
Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

M. J. Chen
Institute for Applied Science and Engineering Research, Academia Sinica, Taipei, Taiwan, Republic of China

L. S. Lee
Electronics Research and Service Organization, Industrial Technology Research Institute, HsinChu, Taiwan, Republic of China

C. W. Liu[a]
Department of Electrical Engineering and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan and Electronics Research and Service Organization, Industrial Technology Research Institute, HsinChu, Taiwan, Republic of China

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The metal–insulator–silicon light-emitting diode (MIS LED) using a high-dielectric-constant material (HfO_2) is studied. The external quantum efficiency for light emission at room temperature from the MIS LED was observed to be 2.0×10^{-6}, as compared to 0.5×10^{-6} for the metal–oxide–silicon (MOS) LED. The large hole concentration at the Si/HfO_2 interface created by the high dielectric constant of HfO_2 may be responsible for the enhancement. The emission line shape of the MIS LED can be fitted by the electron-hole plasma recombination model, similar to the MOS LED. The Al/HfO_2/silicon LED with a high interface trap density has a continuous spectrum below the Si gap beside the electron-hole plasma emission, probably due to the radiative recombination between the electrons and holes via the interface states.
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Due to the indirect band gap of Si, Si-based devices have limited applications on optoelectronics as compared to the direct band gap III–V devices, especially in light-emitting devices. The image sensors[1] and photodetectors[2] based on Si technology have a significant market share of optoelectronics, while few Si-based light sources can reach the practical applications due to the extremely low efficiency ($\sim10^{-6}$). It is interesting to develop the Si light source for the purposes of applications and scientific research. To increase the light-emitting efficiency, the carrier concentration has to be increased, and so does the oscillator strength (matrix element) of the photon emission process for a constant nonradiative lifetime. The carrier accumulation at SiO_2/Si interface in the metal–oxide–silicon (MOS) tunneling diodes could increase carrier concentration in the radiative recombination and the light emission from MOS light emitting device (LED) was demonstrated.[3,4] The oscillator strength of the radiative process can be enhanced by providing an extra momentum conservation mechanism such as the oxide/silicon interface roughness. The emission intensity was reported to be enhanced by the rough Si/SiO_2 interface.[5,6] The high dielectric constant material such as HfO_2 is attractive to the future scaling of MOS field effect transistors.[7–9] We report the emission properties from the metal–insulator–silicon (MIS) tunneling diodes using HfO_2 as gate dielectrics, and compare with SiO_2 devices. The light emission from the MIS structure can be a useful diagnostic tool to characterize the Si/HfO_2 interface.

Two kinds of MIS tunneling diodes were fabricated. Sample A is made by atomic layer chemical vapor deposition (ALCVD)[10] using the $HfCl_4$ precursor and H_2O vapor at 300 °C on 10–30 Ω cm *p*-type wafers. After the deposition, the HfO_2 film was annealed at 600 °C for 60 s in N_2 by rapid thermal annealing. For sample B, the 1 nm oxide was pregrown by rapid thermal oxidation (RTO) on 10–25 Ω cm *p*-type wafers and a 2 nm HfO_2 layer was then deposited by sputtering. The wafer was annealed at 900 °C for 5 min in N_2 by rapid thermal annealing after HfO_2 deposition to create the significant interface trap density (D_{it}) at Si/HfO_2 interface. However, the D_{it} cannot be measured reliably due to the large tunneling current. The D_{it} estimated from the similar sample with a low leakage current is on the order of $1\times10^{12}\,cm^{-2}\,eV^{-1}$. The HfO_2 thickness was measured by transmission electron microscopy (TEM). The MIS LED diode had an Al gate electrode with circular areas defined by

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[a] Electronic mail: chee@cc.ee.ntu.edu.tw

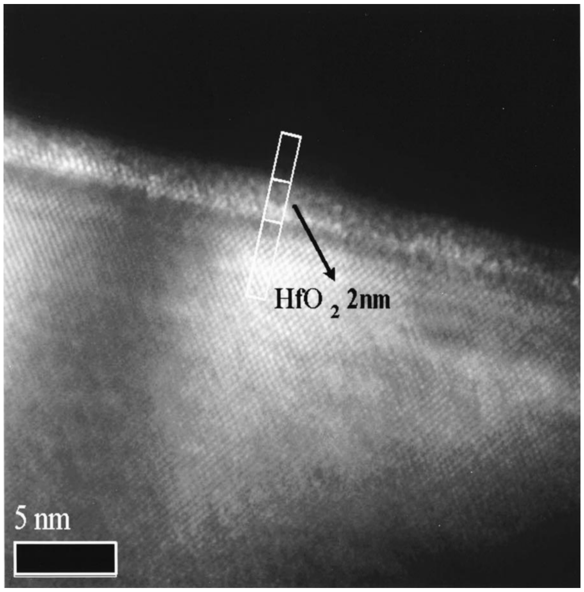

FIG. 1. Cross-section TEM micrograph of HfO_2 on *p*-type Si wafer, after 1 min postdeposition annealing at 600 °C.

the shadow mask. Another Al contact is on the back of the wafer. For comparison, the SiO_2 insulator is also used as gate dielectrics grown by RTO at 900 °C.

Figure 1 shows the cross-section TEM image of 2 nm HfO_2 grown by ALCVD on a *p*-type Si wafer with ~0.6 nm interfacial layer. Figure 2 shows the electroluminescence spectra at the room temperature from sample A with a device area of $4\times10^{-2}\,\mathrm{cm}^2$ at different gate bias. The current to drive the HfO_2 device has a square wave with a period of 30 ms and 17% duty cycle to reduce the sample heating. The light emission intensity is enhanced as the gate bias increases. The electron-hole plasma recombination model[11,12] gives a reasonable fit to the electroluminescence data. The comparison of external quantum efficiency between the HfO_2 device and the SiO_2 device is shown in the inset of Fig. 2. The MIS LED using the HfO_2 shows a high external quantum efficiency of 2×10^{-6} at the current of 100 mA,

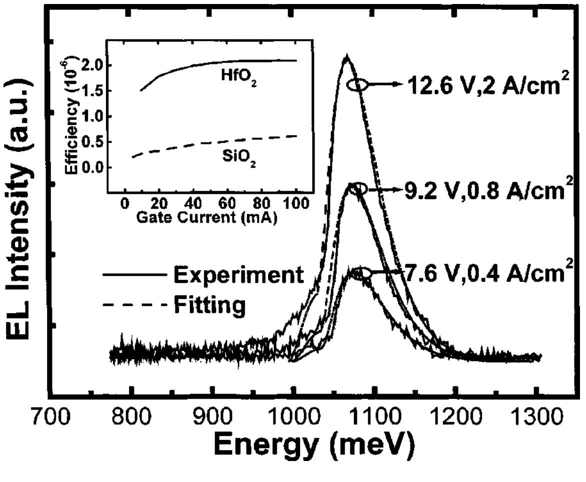

FIG. 2. The measured electroluminescence spectra of HfO_2 LED with the fitting curves by the electron-hole plasma recombination model. The inset shows the external quantum efficiency of the HfO_2 and SiO_2 devices.

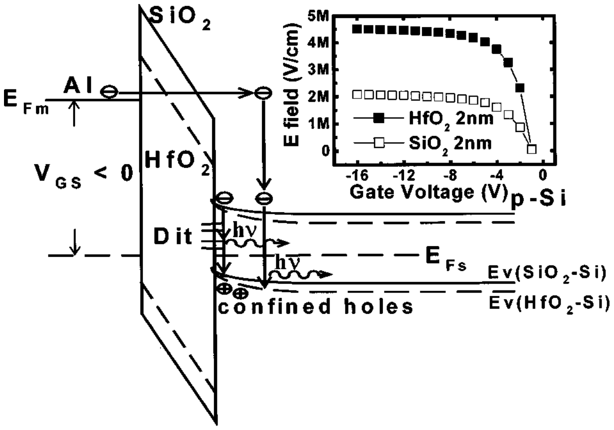

FIG. 3. A schematic energy band diagram of a MIS diode on *p*-type Si wafer at accumulation bias. The dashed line and solid line represent the band alignments of HfO_2 and SiO_2 devices, respectively. The inset is the electric field at different gate bias by numerical simulation.

and the MOS device with 2.3 nm oxide has only one quarter of external quantum efficiency of the HfO_2 device. Note that in our quantum efficiency measurement, we cannot collect all the light from the device, and the number presented here is a lower bound of the true quantum efficiency.

At the accumulation bias, the electrons in the Al gate electrode tunnel to the *p*-type Si through the ultrathin SiO_2 or HfO_2. After relaxation to the conduction band edge, the electrons can recombine directly with the holes at the accumulation region of Si, and recombine with holes via the interface states. If the momentum conservation can be obtained for both processes, the direct recombination of electrons and holes can emit band edge light of Si, and the recombination of the electrons and holes via the interface states can emit light with the energy lower than the Si band gap.

For $Al/SiO_2/Si$ and $Al/HfO_2/Si$ systems shown in Fig. 3, the electron barrier tunneling from Al metal to Si is 3.15 and 1.28 eV, respectively, and the hole barrier tunneling from *p*-type Si to Al electrode is 4.78 and 3.35 eV, respectively.[13,14] For both systems, the electron tunneling barrier is much smaller than the hole tunneling barrier, and the electron tunneling is the dominant current component. At the accumulation bias, most of the gate voltage drops on the insulator of the MIS diode, and thus the electric field in the oxide should be similar to that in the HfO_2, if both have a similar thickness. Due to the high dielectric constant of HfO_2 (~20) as compared to oxide (3.9), the same voltage bias can yield a larger electric flux $D=\epsilon\mathcal{E}$ in the HfO_2. Because of electric flux continuity, the electric field ($\mathcal{E}$) in Si for the HfO_2 device should be larger as compared to the SiO_2 device. The larger electrical field can attract more holes accumulated at the HfO_2/Si interface as compared to the SiO_2/Si interface. The inset of Fig. 3 shows the simulated electrical fields in Si for both the HfO_2 device and the SiO_2 device with the same thickness (2 nm). Therefore, the tunneling electrons from Al gate can have large recombination rate in the HfO_2 device and this yields an enhanced light emission. However, the quantitative analysis is still required for the complete understanding this enhancement effect. For example, the soft phonons[15] in HfO_2 may also enhance the

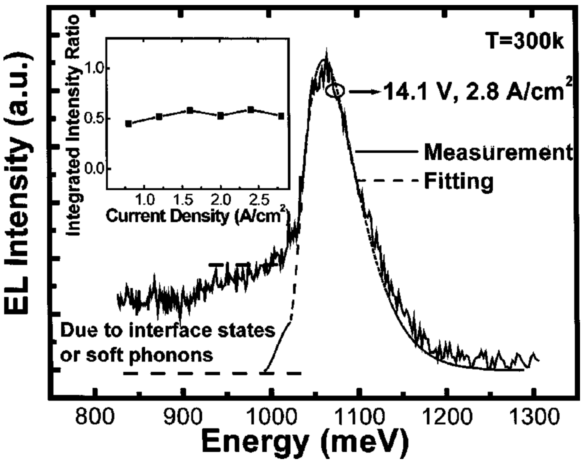

FIG. 4. The electroluminescence spectrum of a HfO_2 LED with a long tail at the energy lower than the Si band gap at room temperature. The inset is integrated intensity ratio vs gate current density.

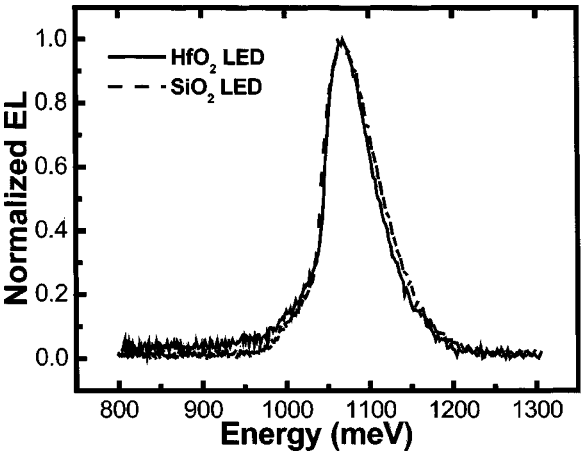

FIG. 5. The comparison of the normalized electroluminescence spectra of the HfO_2 and SiO_2 LEDs.

scattering to conserve the momentum required by radiative recombination. For sample B, intentionally created interface states are obtained by annealing at 900 °C in N_2 with the estimated D_{it} on the order of $1\times10^{-12}\,\mathrm{cm}^{-2}\,\mathrm{ev}^{-1}$. Note that the large tunneling current of the MIS diode (sample B) yields the difficulty to measure the D_{it} accurately. The tunneling electrons can recombine with holes at Si/SiO_2 interface via the interface states. A long tail spectrum (Fig. 4) is observed with the energy lower than the Si band gap. This tail has not been observed in the SiO_2 device probably due to the low interface trap density ($\leqq 10^{11}\,\mathrm{cm}^{-2}\,\mathrm{eV}^{-1}$). However, the soft phonons in HfO_2[15] may also help the radiative recombination via the interface states. The inset of Fig. 4 is the integrated intensity ratio at the different current density. The integrated intensity ratio is the ratio of the integrated intensity in the long tail region to that of the band edge emission due to the electron-hole plasma recombination. The ratio almost does not change with current density, since the band bending of valence band edge does not increase significantly at the increasing accumulation bias, and the electrical field maintains the same at the increasing gate bias (inset of Fig. 4). The line shapes of normalized electroluminescence intensity for SiO_2 LED and HfO_2 LED (sample A) with low D_{it} are basically the same, as shown in Fig. 5. The SiO_2 device has a continuous current excitation, and therefore the device temperature is slightly higher than the HfO_2 device, and this yields a slightly broad line shape at higher energy.

In summary, the light emission from Al/HfO_2/p-Si tunneling diodes has an enhanced intensity of the band edge electron-hole plasma recombination, as well as a long tail spectrum with the energy lower than the Si band gap, which has not been observed in the SiO_2 devices. The high dielectric constant of HfO_2 to increase the hole concentration at Si/HfO_2 interface at the accumulation bias can be one of the origins of the enhancement. The soft phonons in HfO_2 can also play an important role in the radiative recombination process, which is worth doing further investigation.

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