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Enhancing electroluminescence from metal-oxide–silicon tunneling diodes by nano-structures of oxide grown by liquid-phase method

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Abstract

Significant enhancement of electroluminescence (EL) at Si bandgap energy is discovered from metal-oxide–semiconductor tunneling diode on p-type Si with oxide grown by liquid-phase deposition (LPD). The LPD grown oxide has nano-structures with the grain size of 10–20 nm. The nano-structure of oxide causes the simultaneous localization of electrons and holes at the Si/SiO_2 interface, similar to the formation of excitons. This makes the process of the phonon-assisted radiative recombination of electron–hole pair more like two-particle collision than three-particle collision, so increasing the probability of radiative recombination. The measured EL efficiency could be more than 1×10^{-6}.
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1. Introduction

Si is the most important material for integrated circuit (IC) industry. Because of the mature fabrication technology based on Si, it is also highly desired to monolithically integrate electronics and optoelectronics in a single Si IC chip. Unfortunately, this goal is hindered by the difficulty of light emission from Si due to its indirect bandgap nature. Thus many efforts had been devoted to converting silicon to a light-emitting material. For example, porous silicon-based devices [1–3], nanocrystalline Si [4,5], Er-doped Si [6,7], and so on, had been attempted. Recently, metal-oxide–silicon (MOS) structures with the oxide grown by the well-controlled rapid thermal oxidation (RTO) had also been discovered to exhibit significant electroluminescence (EL) at Si bandgap energy [8,9]. Because the structure and processing are completely compatible with current ultra-large-scale integrated (ULSI) circuits technology, it shows promise to achieve the practical silicon-based optoelectronics ICs.

It had been theoretically predicted that the roughness can enhance the visible light emission by a factor of ∼10 in the MOS structures [10]. Recent study with RTO oxide grown at reduced temperature had indirectly proved that

the roughness could also enhance the band-edge EL from the MOS tunneling diode [11]. The roughness scale therein is in the order of 0.5 nm. For such small roughness, its effect is mainly to scatter the carrier and change the carrier momentum. Therefore, the condition for additional momentum required for electron–hole recombination in the indirect bandgap situation is relaxed. In this work, we provide another direct evidence that the obvious roughness of the oxide layer could significantly enhance the EL. The oxide is grown by liquid-phase deposition (LPD). The lateral roughness of the oxide is in the range of 10–20 nm, over one order of magnitude larger than the previous one [11]. With this large-scale roughness, the EL enhancement is even more prominent than the small roughness in the scale of 0.5 nm. The measured external quantum efficiency is more than 10^{-6}. Because the optical power is only measured from the periphery of the MOS structure, the actual EL efficiency should be more than 10^{-5}. The large-scale roughness should provide different mechanisms for enhancing EL on MOS structure. The physics will be discussed.

2. Experimental

Although the oxide grown by LPD had been realized to have good quality [12], the process is actually quite chemically dependent [13]. For the purpose of enhancing EL from the MOS structure, our LPD process is as follows. First,

excess silicic acid ($SiO_2 \cdot nH_2O$) powder was added into a commercially available hydrosilicofluoric acid with 40% of H_2SiF_6 in weight. The solution was stirred for 3 h to ensure full saturation at room temperature. Then this supersaturated solution passed through a no. 2 filter paper so that the unsolved ($SiO_2 \cdot nH_2O$) particles were filtered out. Afterwards, the solution was diluted with 39 times of de-ionized (DI) water in volume. The diluted solution was again stirred for 50 min and then remained quiet for more than 10 min.

The (1 0 0) Si wafers used in the experiment were p-type with the resistivity of 1–$5 \, \Omega$ cm. The wafers were first cleaned with standard processing techniques. Then the native oxide on the Si wafers was removed by buffer-oxide-etchant (BOE). Afterwards, they were put in the prepared solution for the deposition of oxide. After a certain period of time, the samples were taken out of the solution and rinsed with DI water. Circular aluminum pads with thickness of 220 nm were deposited on top of the oxide by evaporation. The other side of those samples was also deposited with Al metal for another electrode.

The thickness was measured on the area without metal pads by ellipsometry. For the sample dipped in the solution for 10 min, the LPD oxide has an average thickness of 1.2 nm, measured by ellipsometry. This oxide layer has nano-structures with a feature size of 10–20 nm. Its photo of field-emission type scanning electron microscopy (SEM) is shown in Fig. 1 and photo of atomic force microscopy (AFM) is shown in Fig. 2. The lateral feature size on AFM photo is about three times the one on SEM photo. Since the resolution of AFM photo is limited by the size of the tip, the lateral feature size shown in SEM photo is more reliable. This layer of oxide with nano-structures turns out to be helpful for EL from MOS structure, as will be explained later. The nano-structures are probably formed due to the local crystallization of the LPD oxide. Two reasons might account for the local crystallization. First, in the preparation of the LPD solution, very tiny particles of unsolved $SiO_2 \cdot nH_2O$ could pass through the pin holes of the filter paper and so are left in the solution. Those particles then di-

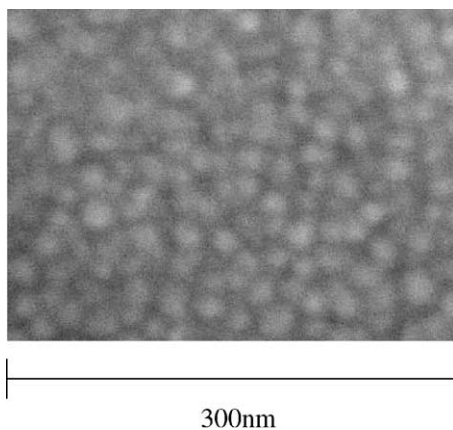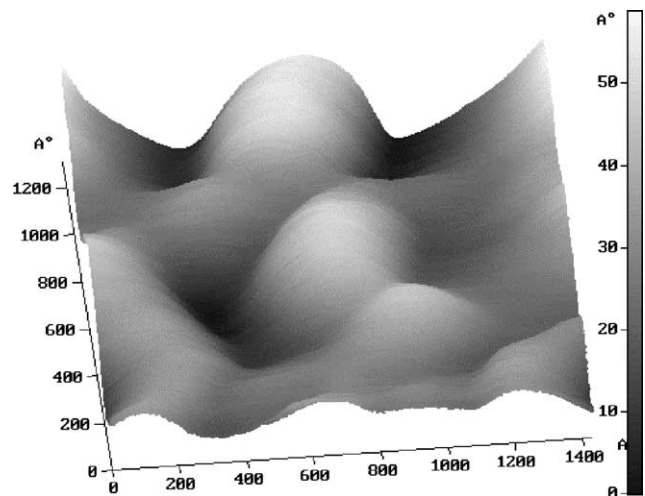Fig. 2. The AFM photo of the LPD grown oxide, showing the vertical deviation.

rectly deposit on the Si substrate. The crystallization starts from those unsolved $SiO_2 \cdot nH_2O$ particles and results in a non-uniform thickness of the LPD oxide layer. Secondly, after the removal of native oxide, the surface of Si wafer is chemically influenced. The top surface probably has either residual oxygen or missing Si atoms, causing non-uniform crystallization of LPD oxide on the Si surface.

3. Results and discussion

Due to the nano-structures, the oxide layer should have varied thickness. The lateral variation is in the range of 10–20 nm based on SEM photo and the height variation is in the range of 4–5 nm as shown by the AFM photo. Although the oxide layer has varied thickness, the MOS tunneling diodes still have good rectification characteristics. Fig. 3 shows a typical J–V curve of the devices. At the 2 and -2 V, the magnitudes of the tunneling current density are 0.62 and $1 \times 10^{-6} \, A \, cm^{-2}$, respectively. Such low reverse-biased current is comparable to the MOS tunneling diode with RTO

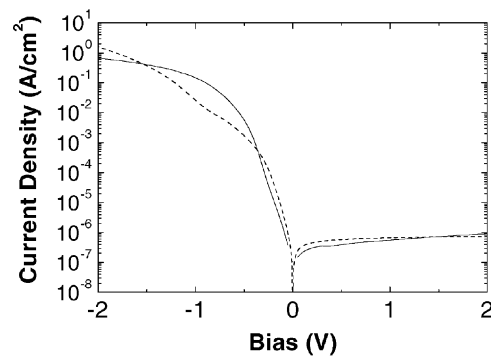Fig. 1. The SEM photo of the LPD grown oxide, showing the nano-structures.

Fig. 3. J–V characteristics of the MOS tunneling diode with LPD grown oxide (dashed line for RTO sample).
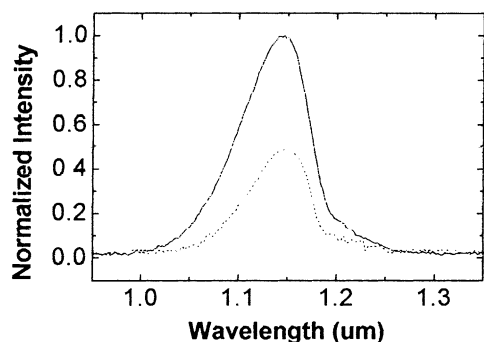
Fig. 4. The measured spectrum (dashed line for RTO sample).

oxide [11], as evidenced by comparison between the solid and the dashed lines. This indicates that the LPD oxide could be as good as the RTO oxide. As a result, there are very small amounts of impurity states and surface states; so the reverse-biased current is very small.

Band-edge EL is observed when the device is forward-biased. No luminescence is observed for the device under reverse bias. The EL spectrum is shown in Fig. 4. The spectrum is measured by the following way. Light from the top of the device is focused by two collimators into monochormator. An InGaAs detector is put at the exit of the monochromator to detect light signal. For comparison, EL spectrum from MOS tunneling diode with RTO oxide is also shown in the dashed line. Their spectral shapes are almost identical except with different power. The comparison of the two spectra shows that similar to the measurement for MOS tunneling diodes with RTO grown oxide, the EL of MOS tunneling diode with LPD oxide corresponds to the bandgap energy of Si. The peak of spectrum is slightly below the bandgap energy of Si at room temperature. This is due to the participation of optical phonon in the radiative recombination [9]. The spectrum could be explained by models including optical phonon, interface roughness, and localized carriers [8,9,11,14].

The L–I curve of the device is shown in Fig. 5. Large-area InGaAs detector is placed very close to the device to measure optical power. The external quantum efficiency at 120 mA of the injection current is 1.9×10^{-6}. This efficiency is
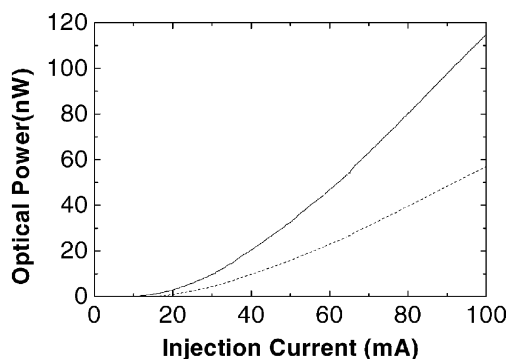
estimated from the optical power measured from the periphery of the bonding pad on the MOS structure. Most of power is still blocked by the silver bonding pad. If the optical power generated from the entire Si/SiO$_2$ interface is collected, the actual EL efficiency should be more than 10^{-5}. The measured efficiency is over two orders of magnitude more than the previous value for the MOS with the oxide grown at 1000 °C [11]. In the previous study, the reduced temperature at 900 °C for RTO grown oxide was proved to increase the surface/interface roughness and so enhance the EL efficiency. In comparison, the efficiency (solid line) shown in Fig. 5 is even more than the value (dashed line) for RTO oxide grown at the reduced temperature [11].

Although both the roughness of the LPD oxide and the roughness caused by reduced RTO temperature lead to the enhancement of EL efficiency from the MOS structure, their scales are very different. In [11], the RTO oxide grown at reduced temperature has the roughness at the scale of around 0.5 nm. The lateral feature of roughness created by the LPD oxide is in the scale of 10 nm, which is more than two orders of magnitude larger. For such large scale of roughness, the momentum change due to the scattering is less than one-tenth of the value in [11], so it is unlikely to provide significant compensation for the large momentum mismatch between electrons and holes in Si. Therefore, the significant enhancement of EL from the 10 nm roughness should be due to other reasons.

The nano-structure shown in SEM photo reveals that the thickness of the oxide layer between Al and Si is not uniform. It could lead to the following two effects. First, the thin oxide region has a stronger voltage gradient than the thick oxide region, so the band bending of Si toward the thin oxide is more severe than the thick oxide for forward-biased condition [15]. This leads to the formation of the potential well along the interface plan in addition to the normal direction. Therefore, in the accumulation region, more holes accumulate in the area where the oxide is thinner. Secondly, more electrons tunnel to Si through the thin oxide layer than through the thick oxide layer. As a result, electrons and holes are coincidentally localized within the same region of around 10 nm, similar to the formation of excitons. The localization of electrons and holes also possibly helps the formation of excitons. Radiative recombination is then enhanced because the process is more like two-particle (phonon vs. electron–hole pair) collision than three-particle (electron, hole, phonon) collision. This also explains why phonon participation is shown in the EL spectrum.

4. Conclusion

Significant enhancement of EL at Si bandgap energy is discovered from MOS with LPD oxide. The oxide could be very thin with an average thickness of 1.2 nm to make the MOS structure behave like a diode with good rectification. Also, the oxide has nano-structures with the lateral variation

Fig. 5. The measured L–I curve (dashed line for RTO sample).

of 10–20 nm and the height variation of 4–5 nm. The enhanced EL efficiency is estimated to be more than 10^{-5}. The enhancement is discussed and attributed to the simultaneous localization of electrons and holes as a result of the nano-structure of the oxide. This causes the process to be more like two-particle collision than three-particle collision, so increase the probability of radiative recombination.

Acknowledgements

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