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Electroluminescence from ITO/SiO_2/Ta_2O_5/Al multiple-layer structure excited by hot electrons

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Abstract

Electroluminescence from indium–tin-oxide (ITO) (200 nm)/SiO_2 (70 nm)/Ta_2O_5 (240 nm)/Al multiple-layer structure is reported for electric field $\geqslant 7$ MV/cm in the SiO_2 layer under alternating current voltage excitation. The SiO_2 and Ta_2O_5 layers are prepared by rf magnetron controlled reactive sputtering. The EL spectrum consists of two bands, a violet–blue band at about 380 nm from the ITO layer when the electrons are injected from the SiO_2 layer to the ITO electrode and a red band at 650 nm from the SiO_2 layer. The intensity of the bands depends on the electric fields in the SiO_2 layer. This field dependence indicates changes in the energy distribution of hot electrons at the ITO–SiO_2 interface and inside the SiO_2 layer.

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1. Introduction

Electron heating in SiO_2 has been studied by three experimental techniques, electroluminescence (EL) [1–3], carrier separation [4,5] and vacuum emission [4,6]. Gradual heating of the electronic carrier distribution was demonstrated for increasing electric fields from 5 to 12 MV/cm with an average excess energy distribution of $\geqslant 4$ eV with respect to the bottom of the conduction band of SiO_2 [4]. EL from radiative decay of metal surface plasmons in n-Si/Si-rich SiO_2/SiO_2/Au or Al electron injector structures, generated by hot electrons from SiO_2 films, was interpreted as evidence for electron heating in SiO_2 [1,2]. Field dependent EL from an indium–tin-oxide (ITO) layer in a similar structure with an ITO electrode instead of Au or Al, was reported for fields from 4.1 to 6.7 MV/cm [7]. Moreover, EL could be generated in bulk SiO_2 [8], if there were luminescent bands in it. This effect was demonstrated by the EL from chemical vapor deposited (CVD) SiO_2 films containing Si islands [8]. EL was attributed to electronic interband transitions in the islands and quantum size effect was proposed as one possible explanation. Luminescent bands in SiO_2 at 1.9, 2.7 and 4.3 eV were reported from photoluminescent (PL) and cathodoluminescent (CL) experiments [9,10]. These bands were assumed to be associated with impurities and defects in SiO_2 [11–14]. However, only few studies have been reported EL bands in SiO_2 to our knowledge.

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2. Experiment

Three EL structures were used in this work, (1) ITO (200 nm)/SiO_2 (70 nm)/Ta_2O_5 (240 nm)/Al (100 nm), (2) ITO (200 nm)/SiO_2 (60 nm)/Ta_2O_5 (240 nm)/SiO_2 (60 nm)/Al (100 nm) and (3) ITO (200 nm)/Ta_2O_5 (240 nm)/SiO_2 (70 nm)/Al (100 nm). The substrates are polished to suppress the light emission from radiative decay of surface plasmons which depends strongly on the surface roughness of the electrodes [1]. The SiO_2 and Ta_2O_5 films were deposited by rf magnetron controlled reactive sputtering in a chamber with two targets of high purity Si and Ta metals. The area of each target was 38.5 × 9.4 cm^2. SiO_2 films were deposited in conditions in which the total pressure was 2 Pa, the pressure ratio of O_2 to Ar was 30%, the rf power was 1000 W and the substrate temperature ranged from 200 to 230°C. The Ta_2O_5 films were sputtered in the same atmosphere as that of SiO_2. The rf power was between 1500 and 1600 W and the substrate temperature was between 230 and 300°C. The back electrode was thermally evaporated Al with a circular area of 3.14 mm^2.

The EL spectra were excited by a 1 kHz sinusoidal wave voltage at constant transfer current. The transfer current was measured by the Chen–Krupka method [15]. I^+ and I^- are defined as the peak transfer current when the Al electrodes are positively and negatively biased. In order to keep I^+ and I^- constant, the applied voltage was gradually increased to compensate for space charge effects due to electron trapping in SiO_2 layers [2,4]. The emitted light was focused on a monochromator, detected by a photomultiplier (Hamamatsu Photonics R456) connected to a recorder. EL decay was measured under excitation of 1 kHz alternating bipolar pulse voltage. The EL signal from the photomultiplier was observed in an oscilloscope. The response time of the detection system was about 1 μs.

3. Experimental results

EL from structures 1, 2 and 3 was detected with the electric fields in SiO_2 above 7 MV/cm. Fig. 1 shows the EL spectra of structures 1 and 2. The spectral structures in the region from 300 to 600 nm are due to optical interference effects because the positions of the peaks shows shifts with changing detective angle and the total thickness of the structures in our samples [16]. The spectra show two bands regardless of the interference effects, a red band at 650 nm (1.9 eV) and a broad violet–blue band from 300 to 600 nm with peak position at approximately 380 nm.

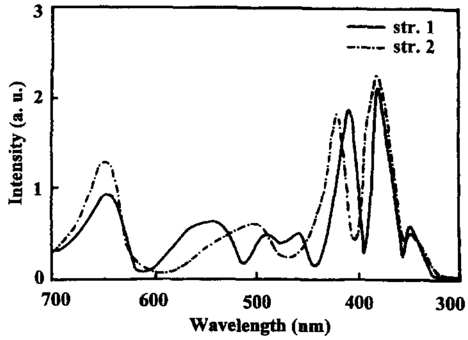

Fig. 1. Room temperature EL spectra of structures 1 and 2. The transfer current $I^+ = 0.25$ mA and $I^- = 0.20$ mA is held constant during the measurement (str = structure).

In order to study the origin of the red band, the EL spectrum of structure 1 is measured at 77 K with the same transfer current, as shown in Fig. 2. The magnitude of the red band in Fig. 2 is about 10 times stronger than that at room temperature. The intensity of the violet–blue band did not change within errors of measurement. The EL decay curve of the red band is measured under excitation by alternating bipolar pulses. The decay curve and its exponential decay

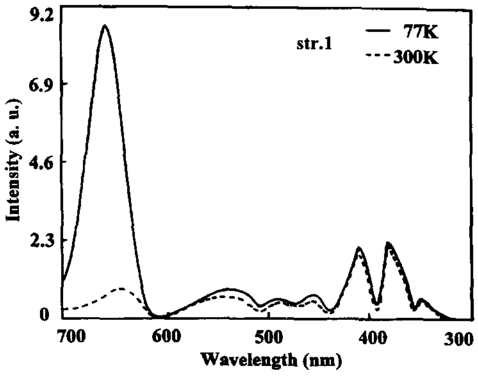

Fig. 2. EL spectra at 77 K and 300 K from structure 1, $I^+ = 0.25$ mA, $I^- = 0.20$ mA.

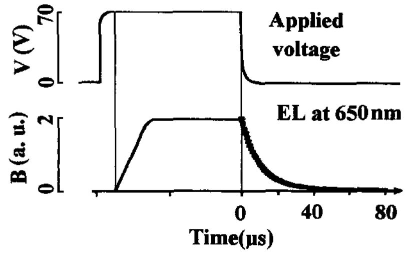

Fig. 3. EL decay at 650 nm at room temperature. The stairs is an exponential decay fitting with $B = 2\exp(-t/9.7)$.

fitting are shown in Fig. 3. It is close to a single exponential decay with decay time of 9.7 μs. There is about 8 μs delay between the applied voltage pulse and the start of linear increase of the EL intensity.

The EL spectrum from structure 3 is measured. In this case a thick Ta_2O_5 layer is used to separate the SiO_2 layer from the ITO electrode. The electric field (≈ 0.7 MV/cm) in the Ta_2O_5 layer is much smaller than that ($\geqslant 7$ MV/cm) in the SiO_2 layer. A decrease of the violet–blue emission in structure 3 is shown in Fig. 4. The dependence of the EL on the polarity of the applied voltage in structure 2 is illustrated in Fig. 5. The waveform of the transfer current is also shown. The polarity dependence of the EL does not depend on the magnitude of the transfer current. The red band at 650 nm exhibits a dependence on voltage polarity. However, the violet–blue band at 380 nm has a larger dependence on voltage polarity, it is very strong when Al electrode is negatively biased (electrons injected from SiO_2 into ITO). The EL from structure 1 shows the same polarity dependence as that from structure 2.

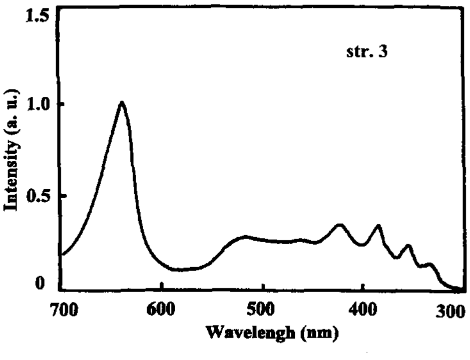

Fig. 4. EL spectrum of structure 3. $I^+ = 0.20$ mA, $I^- = 0.25$ mA.

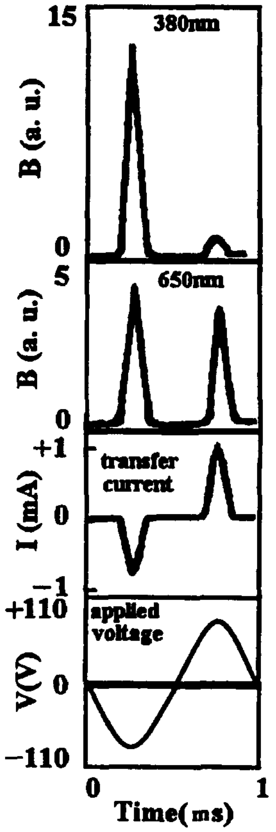

Fig. 5. Polarity dependence of transfer current, EL at 650 nm, EL at 380 nm on the applied voltage in structure 2.

The intensity of EL at 650 and 380 nm is measured alternatively at a constant peak transfer current I^- in structure 1. As current passes through the SiO_2 layer, electrons are trapped in SiO_2 which causes a decrease of the transfer current. In order to maintain the transfer current, the applied voltage should gradually increase to compensate for these negative space charge effects [2,4]. The trapped electrons in SiO_2 cause an increase of the electric field strength $E_i(t)$ near the ITO–SiO_2 interface and also the average electric field strength, $\overline{E(t)}$, in the SiO_2 layer [7]. The determination of $E_i(t)$ and $\overline{E(t)}$ will be given in Section 4. The intensity of the red band at 650 nm is plotted as a function of $\overline{E(t)}$ in Fig. 6. The red band increases gradually and linearly with increasing $\overline{E(t)}$ over the range from 7 to 10 MV/cm. The depen-

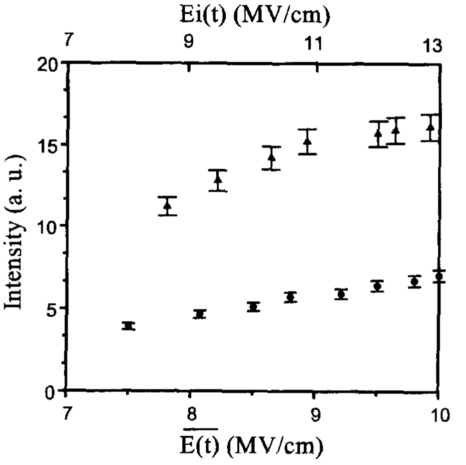

Fig. 6. Intensity of EL as a function of electric field strength in structure 1. The peak intensity of 650 nm band is plotted as a function of $\overline{E(t)}$. The peak intensity of 380 nm band is plotted as a function of $E_i(t)$. The transfer current, $I^- = 1$ mA, is kept constant during measurement.

dence of EL intensity at 380 nm on $E_i(t)$ is also shown in Fig. 6. The intensity of the violet–blue band shows a linear increase with the field $E_i(t)$ from 7 to 10 MV/cm and then is constant with the increase of $E_i(t)$ above 10 MV/cm.

4. Discussion

4.1. The red band

For the red band, the temperature dependence and the decay curve are the same as that of the 1.9 eV (650 nm) luminescent band which has been widely studied by photoluminescent (PL) and cathodoluminescent (CL) methods [9,17]. It has been demonstrated that the red band is associated with the non-bridging oxygen hole centers (NBOHC) in amorphous SiO_2 [10,14,18]. The field dependence of the red band at a constant transfer current shows that the excitation processes are associated with electron heating at high fields ($\geqslant 7$ MV/cm) in SiO_2. Since the 1.9 eV band of NBOHC can be excited by Ar^+ laser (2.41 eV) in the PL study [14] and it has been demonstrated that hot electrons can reach an energy $\geqslant 4$ eV above the conduction band of SiO_2. Electrons with such an energy are sufficient to excite the luminescent band of NBOHC. There is 8 μs delay between the applied voltage pulse and the start of the linear increasing of the EL intensity in Fig. 3. Similar delay of the EL has been reported in other metal–isolator–metal (MIM) structures [19]. This delay is probably caused by dielectric charging of the SiO_2 layer before the threshold electric field strength for EL.

4.2. The violet–blue band

Since a similar violet–blue emission has been reported from the ITO layer in a structure of ITO/SiO_2/Si-rich SiO_2/n-Si [7], we suggest that the strong violet–blue emission mainly comes from the ITO layer or interface between ITO and SiO_2 layers in structure 1 and 2. The similar dependence of the EL intensity on the polarity of the applied voltage in structures 1 and 2 confirm this suggestion. The spectral difference between structures 1 and 3 clearly indicates that the violet–blue band takes place in ITO or near the ITO–SiO_2 interface and depends strongly on electron injection from SiO_2 at high field ($\geqslant 7$ MV/cm). We propose a excitation model in which generation of electron–hole pairs by hot electrons from SiO_2 layer take place in ITO layer and the light emission is produced by radiative recombination processes across the direct band gap via localized states near the band edge. This proposal is supported by the dependence of light emission on structure, voltage polarity and the electric field. Taking account of the barrier height, 4.05 eV, at the ITO–SiO_2 interface [20], hot electrons injected from SiO_2 layer at field > 7 MV/cm have an energy of $\geqslant 8$ eV above the conduction band of ITO. Electron–hole pairs will be generated in the ITO layer by these hot electrons.

4.3. Field dependence

Before discussing the field dependence of the EL in structure 1, $E_i(t)$ and $\overline{E(t)}$ should be determined. We emphasize that no space charge effect is observed in the Ta_2O_5 layer and the transfer current, I^-, is controlled by the electric field at the SiO_2–Ta_2O_5 interface as that in an electron injector structure [2]. By measuring the resistance of ITO/Ta_2O_5 (200 nm)/Al and ITO/SiO_2 (200 nm)/Al structures with the same evaporated Al dot area, we consider that the resistivity of the Ta_2O_5 layer is about one order of magnitude less than that of the SiO_2 layer. So we assume the transfer current, I^-, to be equal throughout structure 1. In the following discussion, only the situation is considered when the Al electrode is negatively biased in structure 1. If $V(0)$ is the initial applied voltage for a constant transfer current, I^-, when no trapping occurs in SiO_2 and the initial field strength $E_i(0)$ near the SiO_2–ITO interface is equal to the average field $\overline{E(0)}$ in the SiO_2 layer; $V_T(I^-)$ is the voltage across the Ta_2O_5 layer which is controlled by I^- and the thickness of Ta_2O_5; $V_S(I^-)$ is the total voltage across the Al–Ta_2O_5 and SiO_2–Ta_2O_5 interfaces for a given I^-; then the initial voltage $V(0)$ can be given as

$$V(0) = \overline{E(0)}l + V_S(I^-) + V_T(I^-), \qquad (1)$$

where l is the thickness of the SiO_2 layer. If the thickness of the Ta_2O_5 is kept constant and the thickness of the SiO_2 layer, l, is varied, $V_S(I^-)$ and $V_T(I^-)$ will not change for a constant I^-. Thus, $\overline{E(0)}$ can be evaluated from the slope of $V(0)$ to l by experiment. Since the transfer current, I^-, controlled by the field strength at the SiO_2–Ta_2O_5 interface is held constant, the applied voltage $V(t)$ had to be gradually increased to compensate for the internal field associated with the trapped charge. Because the trapped charge is uniformly distributed throughout the SiO_2 layer [21], the average electric field $\overline{E(t)}$ in SiO_2 and the relationship between $E_i(t)$ and $\overline{E(t)}$ are given by

$$\overline{E(t)} = \frac{V(t) - [V_S(I^-) + V_T(I^-)]}{l}, \qquad (2)$$

$$E_i(t) = \overline{E(0)} + 2[\overline{E(t)} - \overline{E(0)}], \qquad (3)$$

where the sum of the $V_S(I^-)$ and $V_T(I^-)$ is given by Eq. (1). Thus, the field dependence of the red and violet–blue bands can be obtained by alternately measuring the intensity of the EL at 650 and 380 nm with increase of $V(t)$.

Because the transfer current is held constant, the field dependence of EL from the SiO_2 and ITO layer may become a probe for the change of energy distribution of hot electrons inside the SiO_2 layer and near the ITO–SiO_2 interface. A heating of hot electrons in SiO_2 is shown for the electric fields from 7 up to 10 MV/cm. A steady state electronic energy distribution near the interface between ITO and SiO_2 layers with $E_i(t) > 10$ MV/cm is illustrated by the saturation of the violet–blue band at 380 nm. This effect is consistent with the results reported by using carrier separation technique in the same order of magnitude of the electric field in SiO_2 [4]. From the relationship between $E_i(t)$ and $\overline{E(t)}$, we know that the energy distribution inside SiO_2 does not reach a steady state because the electric field at the SiO_2–Ta_2O_5 interface is held constant. So the intensity of the red band from NBOHC centers in SiO_2 shows a continuous increase with increasing $\overline{E(t)}$, even though the energy distribution of hot electrons at ITO–SiO_2 reaches a steady state. This effect shows that the energy distribution of hot electrons injected from SiO_2 to ITO depends on electron heating in a region close to the ITO–SiO_2 interface.

5. Summary

The red band at 650 nm is demonstrated to be the luminescent band of NBOHC in SiO_2. The violet–blue band is attributed to light emission from the ITO layer. The dependence of the bands on electric fields in SiO_2 is explained by electron heating in SiO_2 with fields of $\geqslant 7$ MV/cm. The field dependence shows a variation of the energy distribution of hot electrons in SiO_2 and near the ITO–SiO_2 interface. An enhancement of the electron heating is demonstrated for fields from 7 to 10 MV/cm in SiO_2 and a steady state energy distribution of hot electrons is shown with fields above 10 MV/cm by the saturation of the EL from ITO layer.

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