Electroluminescence from ZnTe MIS Structure using Natural Oxide as Insulating Layer

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(Received 3 June 2008; Accepted 12 January 2009; Published 4 April 2009)

I. INTRODUCTION

Zinc telluride (ZnTe) has direct band-gap energies about 2.26 eV and this material has high potential for green LEDs. The conduction type of undoped ZnTe is a p-type for its self-compensation effect and it is rather difficult to obtain n-type materials. Therefore, either heterojunctions of ZnTe with other n-type materials or MIS (metal-insulator-semiconductors) have been suggested to the candidates for ZnTe LEDs. After 1998, however, n-type ZnTe materials and their homojunctions have been reported and, at present heterojunctions, homojunctions and MIS structures are three candidate groups for ZnTe green LEDs.

Concerning ZnTe heterostructures, Tsurkan et al. reported electroluminescence (EL) in 1970s [1]. About MIS structures, a number of recent reports focus on either ZnO or ZnMgO. Peiliang et al. found that the MIS structures of Au/SiOx/ZnO on n+ silicon substrates generated detectable EL and that the insulating layer (SiOx) had a critical thickness [2]. Wang et al. formed insulating ZnO layers by the implanting N+ ions into undoped ZnO substrates and very weak UV EL was observed only at 120K [3]. Thus, the reported weak blue/UV EL was obtained either at low temperatures or under significantly high bias voltages (typically several tens of volts) [4]. Generally, EL intensity is not strong enough because of a number of defects at the interface.

Concerning ZnTe homostructures, in 1998, Iodko et al. reported the p-ZnTe/n-ZnTe structure which had the phosphorus-doped p-ZnTe substrate and Al doped n-ZnTe layer by a laser technique, and they observed EL [5]. In 2000, Sato et al. reported EL from the homojunction which had a p-type ZnTe single crystal substrate grown by the vertical gradient freezing (VGF) method and an n-type ZnTe layer. The n-type layer was fabricated by low temperature annealing with covering the surface of the substrate by the deposition of an n-type dopant Al [6, 7]. Tanaka et al. reported I-V characteristics and 550 nm EL at room temperature from LED by using a p-ZnTe substrate grown by the vertical Bridman method and an n-ZnTe layer formed by Al diffusion technique [8]. Neither EL intensity nor its efficiency, however, is satisfactory enough.

Concerning ZnTe MIS structures, in 1970s, Gu et al. reported yellow and green EL from the MIS structures comprising Al impurities [9]. Kennedy et al. reported green and red EL [10]. The MIS devices fabricated from annealed crystals by a technique in which insulating layer was produced by Al and In alloying. Donnelly et al. also observed green and red EL from the ZnTe based avalanching MIS diodes [11]. The high resistivity layer of p-ZnTe is created by using proton bombardment, where the breakdown voltage was 6 V. Ion implantation in ZnTe has been used for fabricating a MIS injection device by Tissot et al. in 1979 [12]. A thin trapping layer and an insulating layer were fabricated by implantation of boron. They observed 550 nm EL at room temperature, and good I-V characteristics.

Generally, the mechanism of EL from MIS structures is explained by impact ionization of carriers within the insulator layers. Thus, insulating layers play key roles in MIS light emitting devices. However, no result is reported about natural oxides of ZnTe as the insulating layer. We focused on the natural oxides (TeO2) of bulk ZnTe substrates and investigated whether or not promis-

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The surface of the ZnTe substrates were degreased by organic solvent, and etched off by diluted NH₄Cl solutions (10%). The surfaces of the substrates were analyzed by XPS before and after the etching. Because natural oxides were suggested to exist on the substrates, Metal-Insulator-Semiconductor (MIS) structures were formed on either as-grown substrates or the etched off substrates as shown in Fig. 1. Ohmic contacts to the etched off substrate surface were formed by using the multi-layers of ZnO and Al. The ZnO layer (500 nm) was deposited by PLD at 250°C and then Al layer (0.4 µm) was deposited by using a vacuum evaporation equipment. Finally, as metal electrodes, Ag paste was put on non-etched surfaces of the ZnTe substrate.

Current-voltage (I-V) characteristics were measured by using a semiconductor parameter analyzer at 300K. The EL spectra were obtained by using a FICS type spectrometer (Oriel, Ltd.) and a Newton type CCD detector (Andor, Ltd). The single acquisition time of the signal was 5 s and the signal integration was done for ten acquisitions.

III. RESULTS AND DISCUSSION

Figure 2 shows the XPS spectra of oxygen and Te on the ZnTe substrate surfaces. Before the etching, a strong oxide spectrum peak was seen at 533 eV [13] in Fig. 2(a). After the etching with the diluted NH₄Cl solutions, the spectrum intensity was significantly decreased to about one-third. Figure 2(b) shows the Te spectra at 573 and
583 eV corresponding to Te and TeO₂, respectively. After the etching, the TeO₂ peaks almost disappeared, and the intensities of the Te peaks were increased significantly by 4 times. Therefore, we conclude that the as-grown substrate surfaces were covered with the TeO₂ layer and that most of the surface layer was removed by the etching. About one third of the oxide spectrum, however, still remained after the etching. This suggests two possibilities: the first is that the surface might be covered with oxygen molecules adsorbed on the surface, and the second is that a new and thin oxide layer was formed during the short time (several minutes) between the etching and the XPS measurement.

Figure 3 shows the current-voltage (I-V) characteristics of Al contact with the deposited ZnO film. A linear I-V characteristic indicates that the contact is Ohmic between the ZnO film and the Al electrode. Figure 4 shows the I-V characteristics of the Ag/TeO₂/ZnTe/TeO₂/Ag (MIS) symmetrical structure. Only a small amount of current flows through the structure and this implies the back to back diode arrangement. Figure 5 shows the I-V characteristics of the final MIS structure, where a clear rectifying characteristic is seen. For the forward bias condition in Fig. 5, the plus voltage was applied on the p-type ZnTe substrate and the lower voltage on the Ag electrode. If a pn junction had been formed between the p-type ZnTe and the ZnO layer, this bias condition with the plus voltage on the ZnO layer and the lower voltage on the p-type ZnTe would have given a reverse I-V characteristic. Therefore, it is suggested that Ohmic contact was formed between the p-type ZnTe and the ZnO layer. Probably, the oxygen-excess TeO₂ layer and the deposited oxygen-deficient ZnO layer might form an alloy at the interface. Consequently, Figs. 4 and 5 indicate that this rectifying characteristic resulted from the Ag/TeO₂/ZnTe (MIS) structure.

Figure 6 shows the EL spectra from the MIS structure at room temperature. The spectrum starts from about 550 nm (green) wavelength. The threshold voltage was about 16 V and the spectrum intensity increased with the forward bias. The emission was strong enough to observe by the naked eyes. Figure 7 shows the integrated intensity of the EL spectra as a function of temperature as shown in Fig. 6.

Figure 8 shows the forward currents at 10 V forward bias voltage as a function of temperature as shown in Fig. 6.
cannot be explained by only a conventional impact ionization model. The EL intensity increased significantly when the forward bias was increased over 16 V. This suggests that another current component, for example, the direct tunneling current, started at the 16 V forward bias voltage. In this tunneling model, if the Fermi energy of Ag electrode reached the conduction minimum of the ZnTe, the electrons might tunnel through the TeO$_2$ from the Ag electrode to the conduction minimum of ZnTe. When the sample temperature was increased, the thermionic hole current should increase but the tunneling current should be almost constant. In the ZnTe region, the hole concentration might decrease because of the increase of the hole current, and the recombination rate might be also decreased. Consequently, as the temperature was increased, the EL was decreased under almost constant tunneling current. Thus, both the tunneling and the thermionic emission currents can explain the I-V and the EL characteristics.

IV. CONCLUSION

The Ag-TeO$_2$-ZnTe MIS structures have been fabricated, and the I-V and the emission characteristics were investigated. The TeO$_2$, the natural oxide of the ZnTe substrates was suggested as the insulating layer. This was shown by the XPS measurement of the substrate surfaces before and after the diluted NH$_4$Cl etching. The MIS structure gave a clear rectifying behavior. Strong electroluminescence (EL) was observed under forward biases at room temperatures; the threshold voltage was about 16 V and the EL intensity increased up to 20 V. The EL spectrum started from about 550 nm wavelength. The forward current increased and the EL intensity decreased as the temperature was increased. Plural current models, including tunneling and thermionic emission currents, could explain both the bias and the temperature dependence of the EL intensities.


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