

## Schottky Barrier Height Reduction for p-ZnSe Contacts by Sulfur Treatment

M. Onomura, S. Saito, J. Rennie, Y. Nishikawa, P. J. Parbrook,  
M. Ishikawa, and G. Hatakoshi

Materials and Devices Research Laboratories, Toshiba Corporation  
1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

telephone: +81 44 549 2141

facsimile: +81 44 520 1802

We have demonstrated the relationship between the structural and electrical properties of the chemically treated p-type ZnSe surface. The unstable Se-rich ZnSe surface, formed by an acid etchant, is shown to be removed by sulfur treatment. The sulfur treatment has been found to have the effect of lowering the Schottky barrier height at the Au/p-type ZnSe interface. This barrier lowering has been found to be effective in reducing the operation voltage of the ZnSe-based devices.

### 1. Introduction

Forming an Ohmic contact to p-type ZnSe is a major problem for the production of blue and green lasers due to its relatively deep valence band edge. A large value of 1.24 eV for the Au/ZnSe Schottky barrier by X-ray photoelectron spectroscopy has been reported previously<sup>1)</sup> and several contact techniques for p-type ZnSe have been studied to reduce the effect of the large valence band offset<sup>2-5)</sup>. Although reduction of this valence band offset to effectively zero has been reported using a Zn(Se,Te) pseudograded structure<sup>3)</sup> and a ZnTe/ZnSe multi-quantum well structure<sup>4)</sup>, the operation voltage is still high, compared to the theoretical value estimated from the energy-gap of ZnSe. Joule heat generated at the poor contact to p-type ZnSe layer affects the degradation of blue/green diode lasers. However, discussion concerning the relationship between the structural and electrical properties of the ZnSe surface, derived from the fabrication procedure, has been lacking to date.

In this paper, we discuss the relationship between the p-type ZnSe surface structure and the barrier height of the Au/p-type ZnSe Schottky contact. The influence of sulfur treatment on the composition of the interface is also discussed.

### 2. Experimental

Fig. 1 shows the schematic structure of a ZnSe-based diode grown by Molecular Beam Epitaxy (MBE) on an n-type GaAs (100) substrate. The diode consists of an n-type ZnSe layer ( $N_d - N_a = 2 \times 10^{18} \text{ cm}^{-3}$ , 2.2  $\mu\text{m}$ ), an undoped  $\text{Cd}_{0.15}\text{Zn}_{0.85}\text{Se}$  single quantum well (SQW) layer (7.5 nm), and a p-type ZnSe layer ( $N_a - N_d = 4.7 \times 10^{17} \text{ cm}^{-3}$ , 1.2  $\mu\text{m}$ ). MBE growth was performed at a substrate temperature of 270  $^{\circ}\text{C}$ , and monitored by reflection high energy electron diffraction (RHEED) to maintain Zn-rich conditions. The p-dopant was plasma-excited nitrogen. The net carrier concentrations of the layers were determined by capacitance-voltage

measurements.

After growth, one of two surface treatments was applied to the p-ZnSe surface. Sample A was etched in an SH etchant -  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  solution - for 1 min at 4  $^{\circ}\text{C}$ , rinsed in purified water, and then dried with  $\text{N}_2$  gas. Sample B was etched in the SH etchant, rinsed in water, dipped in a 1 g  $\text{P}_2\text{S}_5$  dissolved in 50 ml  $(\text{NH}_4)_2\text{S}$  solution for 1 min at room temperature<sup>6,7)</sup>, rinsed in water, and then dried. The  $\text{P}_2\text{S}_5:(\text{NH}_4)_2\text{S}$  solution is alkaline, thus a water rinse after the SH etching is necessary prior to the sulfur treatment. No anomalous surface morphologies after the surface treatments for samples A and B were observed by Nomarski contrast microscopy.

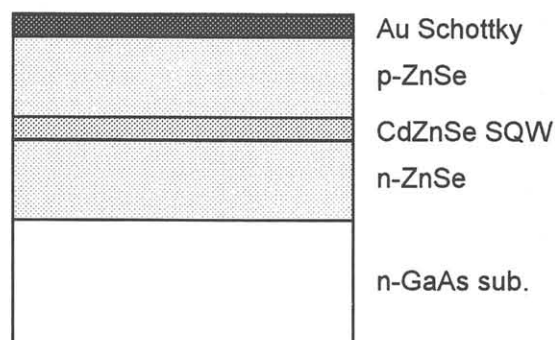


Fig. 1 Schematic structure of the ZnSe-based diode.

The surface composition of each sample was observed by Auger electron microscopy (AES) after surface treatment. The current-voltage (I-V) characteristics were evaluated after evaporating Au Schottky metal on the treated p-type ZnSe layers. The estimation of the barrier height at the Au/p-type ZnSe interface was made using the model of Suemune<sup>8)</sup>, considering the thermionic emission and tunneling currents in the diode structure.

### 3. Results and discussion

#### 3.1 Surface property of the sulfur treated ZnSe

Fig. 2 shows the surface compositions of samples A and B by AES. Peak signals from zinc, selenium, oxygen, carbon, sulfur, and phosphorus were observed in both cases. The carbon peak was decreased dramatically by the sulfur treatment, although that of oxygen was increased slightly. The phosphorus signal was nearly identical in both cases. The surface compositions of the observed elements for samples A and B are listed on Table 1. The relative proportion of the observed elements was estimated from the ratio of the peak intensities. For sample A, the zinc content decreased, and the Zn/Se ratio was 0.85. In contrast, a value of Zn/Se=1.02, nearly equal to that of bulk ZnSe grown by the MBE, was found for the sulfur treated sample (B). These results suggest that by using the sulfur treatment, residual selenium on the surface is removed and a surface close to stoichiometry is obtained. Furthermore sulfur treatment may be an effective procedure in order to regrow Zn(S)Se on a Zn(S)Se surface to obtain for example a buried current confinement structure for a high efficiency laser diode.

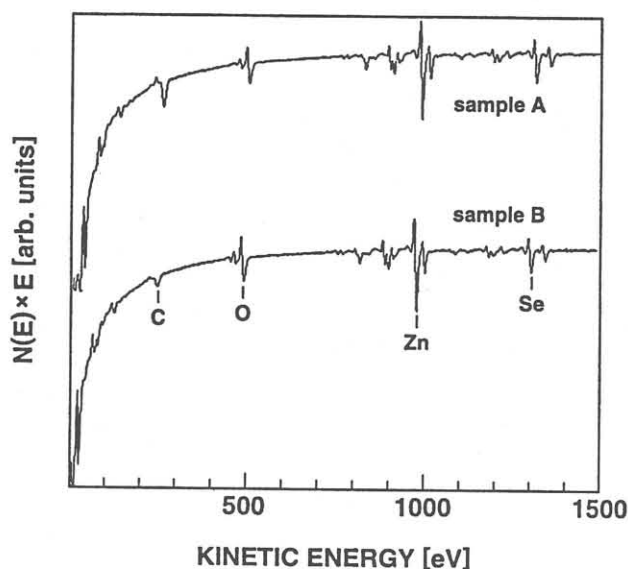


Fig. 2 Surface properties of samples A and B

Table 1 The estimated surface compositions of samples A and B

Sample	Carbon	Oxygen	Phosphorus	Sulfur	Zinc	Selenium	Zn/Se
A	10.16 %	4.71 %	3.21 %	0.85 %	37.34 %	43.73 %	0.85
B	5.56 %	6.70 %	3.19 %	1.06 %	42.15 %	41.34 %	1.02

For comparison, we applied the same process used for sample B to a ZnSe wafer grown by the vertical Bridgman method<sup>9)</sup>. It is known that when a bulk ZnSe wafer is dipped in an acid based etchant like SH, the surface reddens. We have found that this red surface, obtained under the SH etchant, returns to *normal* on surface treatment using sulfur within a few seconds. This suggests that the residual selenium causes reddening of the ZnSe surface.

#### 3.2 Estimation of the barrier height

Au Schottky contacts, as shown in Fig. 1, were formed to the ZnSe surface immediately after the surface treatments. The experimental room temperature I-V characteristics for samples A and B are plotted in Fig. 3. The solid lines are the calculated I-V characteristics. The parameters used for the calculation were  $m^*/m=0.6$ ,  $\epsilon_s/\epsilon_0=8.6$ , and the actual acceptor concentration of  $4.7 \times 10^{17} \text{ cm}^{-3}$ . When the diode is forward biased, the Au/p-type ZnSe interface is reverse biased. The forward biased ideal diode current for the p-n junction is very high so the diode current will be equal to the sum of the thermionic emission current and the tunneling current flowing from the metal to the p-type ZnSe. The tunneling current dominates the calculated I-V characteristics in the high voltage region. The barrier height of the Au/p-type ZnSe interface was estimated from the Schottky reverse biased I-V characteristics. The details of the p-type ZnSe/CdZnSe/n-type ZnSe heterostructure was not taken into account in the actual calculation.

The estimated barrier height of Au/p-type ZnSe is 0.75 eV for sample A, and 0.6 eV for sample B. In particular, the calculated I-V characteristics for sample B are in excellent agreement with the experiment over a wide voltage range. The difference between the calculated line and the experimental data of sample A may be caused by the effective contact area, derived from the effective Richardson's constant. This deviation may be related to the Se-rich surface, obtained under the SH etchant: it was noted the experimental I-V characteristics of sample A tended to be unstable with time.

The estimated barrier heights seem to be too low compared to the generally accepted value of 1.24 eV. On the other hand, the barrier heights of these samples are consistent with that reported by Suemune<sup>8)</sup>, who proposed

the calculation to obtain a fit to the I-V characteristics of the first reported ZnSe-based laser by Haase et al of 3Ms<sup>10</sup>. The reason for the underestimation compared to the generally accepted value is that the barrier height is probably being influenced by the interface structure, or that the effective barrier height of this interface is truly lower than the value of 1.24 eV. The Schottky effect is one possibility for the lowering, but this effect is very small of the order of 0.1 eV.

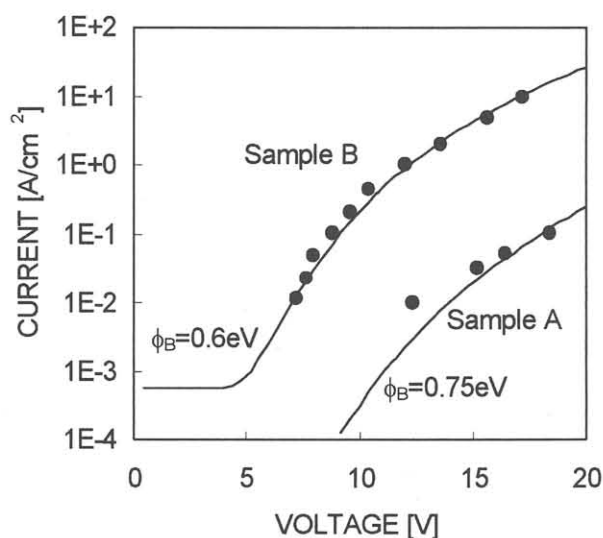


Fig. 3 Experimental I-V characteristics for Au/p-type ZnSe Schottky diodes with and without sulfur treatment (circles). Calculated fits are also shown (solid curves).

It is technically difficult to eliminate interfering surface states caused by contamination by oxygen, carbon etcetera. The oxygen content was slightly increased by the sulfur treatment, but the barrier height was decreased. The sulfur treatment has the effect of lowering the barrier height despite any included contamination. In addition, the sulfur treatment was found to have the effect of stabilizing the I-V characteristics. Therefore the barrier lowering caused by the sulfur treatment is also effective in not only reducing the operation voltage in ZnSe-based diode lasers but also improving the reproducibility of the electrical characteristics.

#### 4. Summary

We have showed the relationship between the structural and electrical properties of the p-type ZnSe surface. The Se-rich ZnSe surface, obtained under an acid etchant, was shown to be removed by sulfur treatment. The sulfur treatment has been found to have the effect of not only returning the ZnSe surface to the intrinsic composition, but also of lowering the Schottky barrier height at the Au/p-type ZnSe interface. This Schottky barrier lowering is also effective in reducing the operation voltage of the ZnSe-based devices.

#### Acknowledgments

The authors would like to thank M. Azuma and M. Nakamura for their continuous encouragement.

#### References

- 1) M. Vos, F. Xu, S. G. Anderson and J. H. Weaver, *Phys. Rev. B* **39** (1989) 10744.
- 2) Y. Lansari, J. Ren, B. Sneed, K. A. Bowers, J. W. Cook Jr. and J. F. Schetzina, *Appl. Phys. Lett.* **61** (1992) 2554.
- 3) Y. Fan, J. Han, L. He, J. Saraie, R. L. Gunshor, M. Hagerott, H. Jeon, A. V. Nurmikko, G. C. Hua and N. Otsuka, *Appl. Phys. Lett.* **61** (1992) 3160.
- 4) F. Hiei, M. Ikeda, M. Ozawa, T. Miyajima, T. Ishibashi and K. Akimoto, *Electron. Lett.* **29** (1993) 878.
- 5) M. Onomura, M. Ishikawa, Y. Nishikawa, S. Saito, P. J. Parbrook, K. Nitta, J. Rennie and G. Hatakoshi, *Electron. Lett.* **29** (1993) 2114.
- 6) J. Bennett and J. A. Dagata, *J. Vac. Sci. Technol. A* **11** (1993) 2597.
- 7) S. Saito, Y. Nishikawa, M. Onomura, P. J. Parbrook, M. Ishikawa and G. Hatakoshi, *Jpn. J. Appl. Phys.* **33** (1994) L705.
- 8) I. Suemune, *Appl. Phys. Lett.* **63** (1993) 2612.
- 9) H. Yoshida, T. Fujii, A. Kamata and Y. Nakata, *J. Cryst. Growth* **117** (1992) 75.
- 10) M. A. Haase, J. Qiu, J. M. DePuydt and H. Cheng, *Appl. Phys. Lett.* **59** (1991) 1272.