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Comparison of Electrical and Optical Properties of n-i-i and p-n ZnSSe Heterostructure Diodes

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Contribution of p-type doping to ZnSSe heterostructure diodes was discussed by comparing electrical and optical properties of n-i-i and p-n diodes grown by metalorganic vapor-phase epitaxy. Although the current flow was observed in the n-i-i heterostructure, red-shift of electroluminescence peak was observed for the higher bias. This was interpreted to be the Stark shift due to the electric field applied to the quantum well structure in the n-i-i diode. The current flow in p-n diodes showed much lower-voltage operation, much better than that of the blue-green laser diode reported by 3M.

1. Introduction

Most of blue or blue-green II-VI laser diodes reported up to now showed laser operations at low temperature of ~77K[1]. Since activation energies of acceptors in ZnSe are ~110meV[2] and are relatively large, hole concentrations at this temperature are extremely low. Then, there arises a question how current flows in this circumstance. A n-i-i heterostructure is a kind of simulation to p-n diodes at low temperature.

In this paper, electrical and optical properties of n-i-i ZnSSe heterostructure diodes were studied to examine the current injection processes. The observed properties are compared with those of p-n heterostructure diodes. The effect of doping is discussed considering these comparisons.

2. Properties of n-i-i ZnSSe Heterostructure Diodes

Both n-i-i and p-n ZnSSe heterostructure diodes were grown by atmospheric-pressure metalorganic vapor-phase epitaxy (MOVPE) at 560℃ on (001) GaAs substrates. The flow rate of DEZn and DESe were fixed to 0.45 and 2.5 μmol/min, respectively. The flow rate of DES was dependent on the S mole fraction in ZnSSe and was, for example, 2.4 μmol/min for the growth of $ZnS_{0.09}Se_{0.91}$.

Figure 1 shows the n-i-i heterostructure studied. The active layer consists of a ZnSe(10nm)/$ZnS_{0.06}Se_{0.94}$ (10nm) multiple quantum well (MQW) structure with 5 wells. ZnSe(5nm)/$ZnS_{0.18}Se_{0.82}$(5nm) superlattice structure with the total thickness of 1 μm was used as the lower cladding layer. Growth of this superlattice structure improves the crystalline properties of the upper grown active layer[3]. Iodine was doped in this superlattice structure using ethyliodide(EtI) for n-type conductivity[4]. The electron concentration was $\sim 7\times10^{17}cm^{-3}$. The upper cladding layer was an undoped $ZnS_{0.09}Se_{0.91}$ with the thickness of 0.85 μm.

Figure 2 shows the current-voltage (I-V) and capacitance-voltage (C-V) characteristics measured on the n-i-i diode at room temperature. The build-up voltage was ~5V for the current density of ~1 A/cm^2 even for this semi-insulating upper cladding layer. The C-V characteristic shows that the upper cladding layer

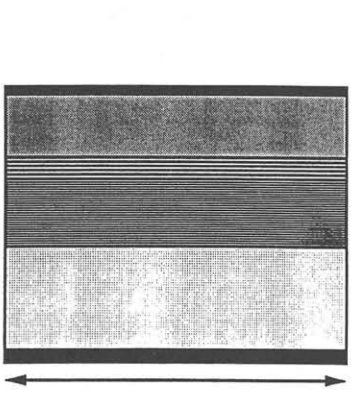

Fig.1. n-i-i ZnSSe heterostructure diode grown by MOVPE.

is completely depleted and the capacitance remained almost constant. The width of the depletion layer estimated from the measured capacitance was ~850 nm. This is shorter than the total thickness of 950 nm in the insulating layers. This result suggests that the iodine doped in the lower cladding layer diffused or segregated during the growth up to ~100 nm in the upper layers probably due to the high growth

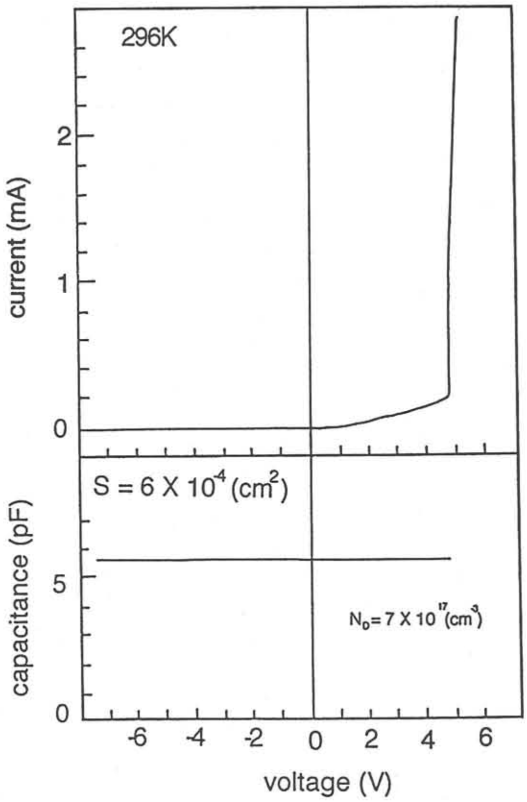

Fig.2. I-V and C-V characteristics measured on n-i-i diode at room temperature.

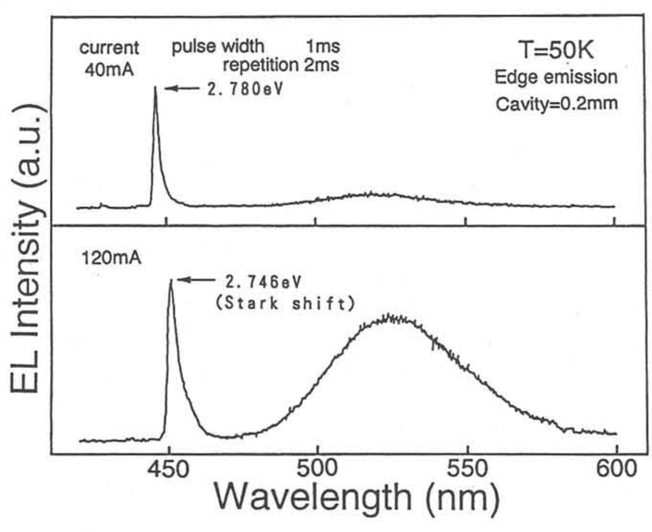

Fig.3. Luminescence spectra from n-i-i diode measured at 50K.

temperature. Therefore the whole active layer may be doped n-type unintentionally. This plays a role in the interpretation of luminescence properties with current injection.

Figure 3 shows the luminescence spectra measured at 50K. The sample had the cavity length of 0.2 mm and luminescence was observed from the cleaved facet. The diode was operated with the 500Hz repetition with the pulse duty ratio of 50%. The blue luminescence was observed as shown in Fig. 3. At the bias current of 40 mA, the luminescence peak was observed at 2.780eV, but this may be affected by the internal self-absorption. At the higher bias current, the luminescence peak showed red-shift. At the bias current of 120 mA, the shift up to 34 meV was observed and also the mid-gap luminescence was increased. The diode voltages for these operations were more than 20 V.

The above-observed phenomena were interpreted considering the band diagram shown in Fig. 4. From the C-V measurement shown in Fig. 2, segregation or diffusion of iodine into the MQW active layer was suggested. Then the band diagram in thermal equilibrium will be like the upper one. With forward bias, the electric field will be induced in the depleted i-cladding layer, and holes are injected thermionically from the upper electrode over the Schottky barrier. The injected holes will drift toward the MQW active layer with the electric field in the i-cladding layer.

At the moderate bias, the energy band around the

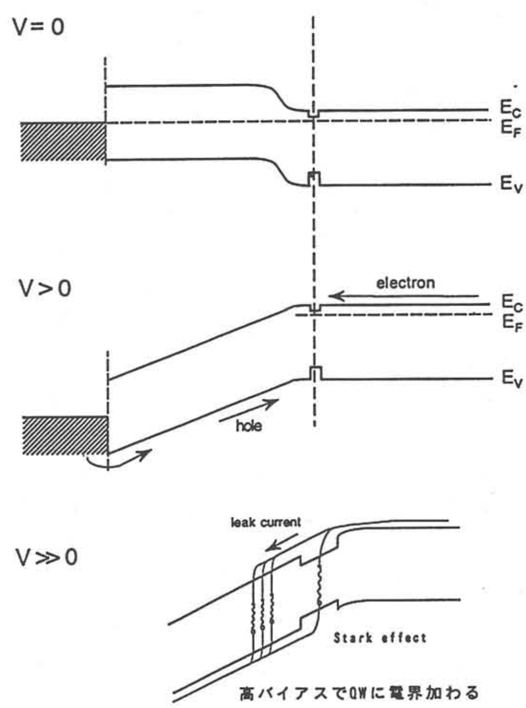

Fig.4. Band diagram to interpret the measured electrical and optical properties in n-i-i diode.

MQW active layer will be nearly flat due to the iodine doping. Therefore the accumulation of the injected electrons and holes in the MQW is possible, which resulted in the observation of luminescence. At the higher bias, however, the depletion layer expands to the MQW active layer and the electric field in the MQW induces the Stark effect on the observed luminescence. The presence of the electric field in the MQW region induces the electron current flow toward the i-cladding layer. This may result in the midgap luminescence observed at the higher bias due to the poor crystalline quality of the i-ZnSSe cladding layer.

These studies suggest the following three points. (1) The transport of carriers in frozen p-ZnSe layers is possible by a drift current as shown in the above experiment. (2) Although the active layer was n-doped in the present experiment, the interpretation based on the band diagram shown in Fig. 4 also suggests the importance of the doping profile around the active layer for the control of the potential distribution. Even if the holes are freezed in the p-ZnSe layer, the Fermi level is fixed at the acceptor level. This controls the band bending around the active layer under forward bias. (3) Under the forward bias to p-n junctions, metal/p-ZnSe contacts are reverse biased. This will cause the ionization of the frozen p-ZnSe from the contact toward the p-n junction. With reasonable p-doping, this will prevent the application of the electric field to the active layer as was observed in the above experiment.

3. Properties of p-n ZnSSe Heterostructure Diodes

A p-n ZnSSe heterostructure diode was grown by MOVPE. Nitrogen was doped in p-ZnSSe layer by introducing thermally decomposed tert-buthylamine (tBA)[5]. In the diode structure similar to that in Fig. 1, nitrogen was doped in the upper cladding layer. From the C-V measurement, the net acceptor concentration, N_a-N_d, of 1~2x10^{16}cm^{-3} was estimated. The I-V characteristic measured at room temperature is shown with closed circles in Fig. 5. The open circles are the reproduction of the I-V characteristic measured on the blue-green laser diode reported by 3M[1]. The drastic improvement of the I-V characteristic in the present diode grown by MOVPE will be clear. The physical origin of this improvement is now under study, but this suggests the possibility of low voltage operations in p-n diodes grown by MOVPE.

Blue luminescence was observed from this diode with the bias current of 20 mA. The corresponding diode voltage was ~2V and was much reduced in comparison to the above n-i-i diode structure.

4. Conclusions

From the comparison of properties of n-i-i and p-n ZnSSe heterostructure diodes grown by MOVPE, the current injection processes were discussed. The I-V characteristic measured in the n-i-i diode suggested that the transport of carriers in frozen p-ZnSe layer at low temperature is possible by a drift current. It was also indicated that the doping profile around the active layer is important for the control of the potential profile to have adequate carrier confinement to the active layer. The p-n diode showed much lower voltage operation than that of n-i-i diode, demonstrating the p-doping effect on the diode voltage reduction.

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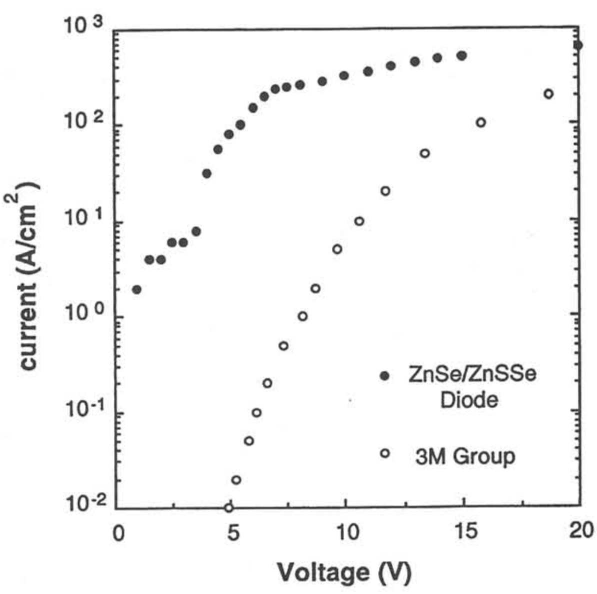

Fig.5. I-V characteristic measured on p-n ZnSSe heterostructure diode at room temperature.