Lasing of exciton at room temperature in ZnO quantum dots thin films

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High quality ZnO thin film was grown by the laser molecular beam epitaxy technique on sapphire (0001) substrate. The lateral grain size was about 50 nm in diameter. Under the high density excitation, exciton-exciton collision process (P line) was observed. From the edge of the sample, very rapid increase of the P line was observed with the increase of the excitation power. A fine structure that comes from the cavity mode was also observed. These facts suggest the lasing of the exciton at room temperature.

The luminescence properties of wide-band-gap semiconductors is currently of considerable interest because of their relevance to the development of short-wavelength diode lasers which are needed in many areas of high-tech. applications. The availability of high-quality MBE grown ZnSe-based semiconductor heterostructures and MOCVD grown GaN has made possible to fabricate blue and blue-green laser diodes.[1,2)]

We report here the strong room-temperature luminescence ant lasing from high-quality ZnO thin quantum dot films grown on sapphire substrates using the laser molecular beam epitaxy (MBE) method.[3,4)] The facet of the ZnO dot plays an important role in the exciton lasing at RT.

Laser MBE is a process especially useful for epitaxial layer-by layer growth of metal oxide thin films[5)] directly from sintered ceramic targets. Laser MBE has some merits for fabricating oxide hetero-structures compared with such growth methods as MBE, sputtering, and metal organic chemical vapor deposition (MOCVD), such as, high energy density, wide applicable pressure range, and simple setup.

ZnO films were grown by originally designed laser MBE equipped with reflection high energy electron diffraction (RHEED). In-situ RHEED observations enable us not only to examine surface structure but also to monitor and control layer-by-layer growth by following the diffraction pattern intensity oscillations. A diffusion pump equipped with a liq. N_2 trap was employed , since it is convenient to use and durable against oxidant gases. The background pressure was better than 1×10^{-7} Pa. At growth temperatures ($\sim$ 600 °C), the background pressure was as low as 5×10^{-7} Pa. Ceramic ZnO target (99.999%) were placed in the chamber and ablated with KrF excimer laser (254 nm, 10 Hz, 20 nsec) pulses focused into a spot of 0.5×2 mm with a fluence of 0.6 J/cm^2. Sapphire(0001) substrates polished on both sides were mounted on a holder, which was placed about 50 mm away from the target. Ultra pure oxygen (99.9999%) was introduced into the chamber with the partial pressure ranging from 1×10^{-4} Pa to 1 ATM. The film was deposited at a temperature of 550 °C in 1×10^{-4} Pa. Torr of oxygen with a deposition rate of 5×10^{-3} nm/pulse. The film thickness was controlled and varied between 50 nm and 500 nm.

RHEED patterns had sharp streak from the beginning of deposition, indicating epitaxial growth. By the X-ray diffraction patterns, only ZnO(00l) peaks were seen along with the sapphire(000l) peaks indicating that the C axis of the ZnO film is perpendicular to the surface of the substrate. A LEED pattern of the ZnO film basal plane showed a well-defined hexagonal lattice. The in-plane crystal orientation relationship was confirmed to be ZnO(1120)//sapphire(1100) from LEED pattern. In this orientation relationship, a lattice mismatch between ZnO and sapphire corresponds to 18.3% at room temperature.

Figure 1 shows an AFM image of the 50 nm-thick film. We can see hexagonal-shaped nanocrystals assemble close to each other. The facet of a ZnO hexagon corresponds to the {1100}plane. This faceted structures strongly contribute to the room temperature lasing of the exciton, as discussed later.

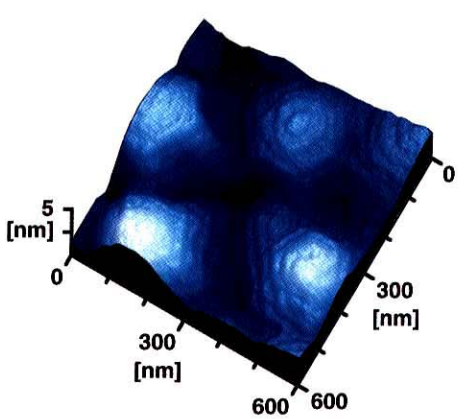

Fig. 1. An AFM image of the ZnO quantum dot thin film with a thickness of 55 nm.

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The thinner the film was, the smaller the lateral nanocrystal became. When the film thickness is 55 nm, the average of the crystal size is 45.2 nm in diameter with ratio of the distributing width to the average size of 33%. The size distribution of these nanocrystals were similar in many observed areas, suggesting that ZnO nuclei coalesced homogeneously on the whole substrate surface.

Figure 2 shows the temperature dependence of the luminescence and absorption spectra obtained from a 50 nm thick ZnO film at low pumping intensity provided by the 325 nm output of a 20 mW He-Cd laser. At temperature below 70 K, a bound exciton line is dominant and no deep luminescence center was observed. At around 100 K, free exciton luminescence appears and shifts to lower energy as a result of the temperature dependence of the band gap energy. This luminescence line is observed up to room temperature. The A and B exciton absorption bands are also observed from low temperature to room temperature. At around 100 K, the absorption and luminescence peaks has the same energy showing that the free exciton luminescence is observed. At room temperature, the absorption peak of the A exciton is still the same as that of the luminescence. In this sample, the exciton survives up to room temperature.

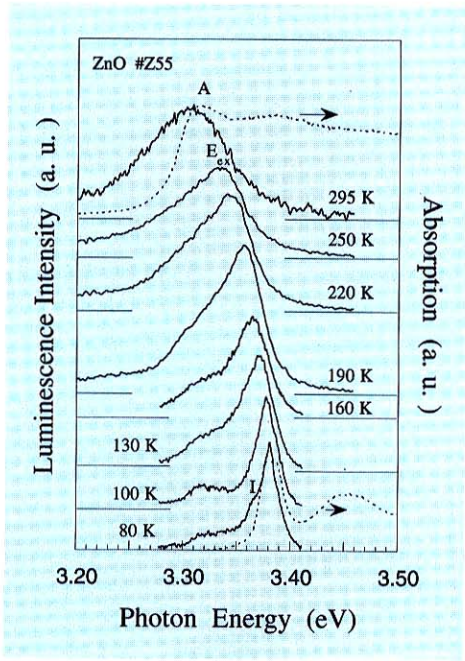

Fig. 2. Photoluminescence spectrum excited by the 325 nm line of a cw He-Cd laser at various temperatures. Eex and I are the free A-exciton emission and neutral acceptor bound exciton emission, respectively. Dashed lines show the absorption spectram.

When the sample was excited by short pulse laser (355 nm 15 ps), strong emission lines P_2 and P were observed. In the bulk crystal, these lines appear at low temperature by the exciton-exciton collision process.[6] In our sample, on the other hand, these P_2 and P lines were clearly observed up to room temperature.

When the emission spectrum was observed from the side of the sample, we found a threshold of the increase of the intensity with the increase of the excitation density. Also some fine structures were observed in the emission spectra of the P line. The separation of these fine structures is proportional to the inverse of the excited length of the sample, that is, these fine structures come from the cavity mode of the Fabry-Perot etalon. The existence of the threshold and cavity mode clearly shows that the ZnO film are lasing by the exciton-exciton collision process. The facet of the hexagon dot strongly affects, as shown in Fig. 3, the intensity of the lasing. When the sample was excited as the excited line pattern perpendicular to the facet, the lasing is strong. But when the excitation pattern was rotated by 30 degrees, the intensity decreased and lasing was stopped.

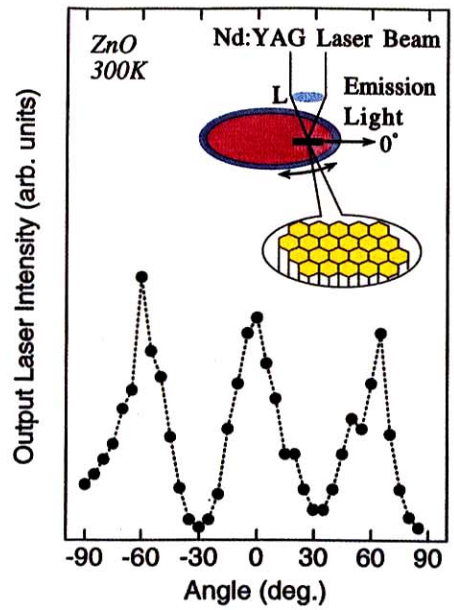

Fig. 3. P-band intensity as a function of the angle between pumping stripe pattern and in-plane crystal axis. 0 degree corresponds the ZnO [1100] direction. The inset depicts the experimental configuration.

In conclusion, we found the room temperature laser operation of ZnO quantum dot thin films. The lasing mechanism is the exciton-exciton collision process. The facets of the hexagonal dots observed at the surface of the film contribute to the low threshold of lasing.

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