Electronic structures of polycrystalline ZnO thin films probed by electron energy loss spectroscopy

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The microstructure of polycrystalline ZnO thin films grown on amorphous fused quartz has been studied by transmission electron microscopy and electron energy loss spectroscopy (EELS). The optical functions of the grain and grain boundary of ZnO acquired from EELS are compared to elucidate the mechanism of the formation of self-assemble laser cavities within this material. It is found that the refractive index of the grain boundary is significantly lower than that of the grain due to the lack of excitonic resonance. This large refractive index difference between the grain and grain boundary substantiates the scenario that the formation of laser cavities is caused by the strong optical scattering facilitated in a highly disordered crystalline structure. In addition, our results also imply that the optical characteristics of ZnO have very high tolerance on defects. © *2000 American Institute of Physics.* [S0003-6951(00)01636-3]

Semiconductors have gained a wide spread of application in light-emitting devices such as light-emitting diodes (LEDs) and lasers.[1,2] Throughout the history of semiconductor, much effort has been devoted to improving the perfection of the semiconductor crystals and in particular to reducing the concentration of intrinsic material defects. It is widely believed that defects in semiconductor lasers degrade their optoelectronic performance as well as lifetime.[2] In today's semiconductor industry, the common practice of making desirable semiconductor involves the concept of heteroepitaxy by growing single-crystal-like semiconductor on foreign substrate.[2] Good epitaxy on single crystal substrate reduces the generation of defects in the materials during the process of deposition and therefore produces high quality semiconductors. Amorphous substrates are seldom used because they do not support epitaxy. The growth of semiconductors on amorphous substrates always leads to polycrystal-like structures that are accompanied with a significant amount of defects. In addition, grain boundaries in polycrystals enhance optical loss in lasing medium. Hence, the use of polycrystalline semiconductor on amorphous substrate for lasing structure is basically considered as an unrealistic concept. However, we recently have demonstrated that laser action can indeed be observed in polycrystalline ZnO thin films.[3] Coherent backscattering[3] on ZnO films that has estimated the mean free path is an order of the emission wavelength of ZnO suggesting the occurrence of strong optical scattering in this material.[3] It is indicated that this scattering could lead to the formation of self-assemble laser cavities in polycrystalline ZnO films, which is not observed in single crystalline material. This phenomenon has motivated the interest of finding the sites where light scattering actually takes place. In this letter, we report the detail studies of the structural and electronic properties of the ZnO thin films by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) to substantiate the light scattering scenario. Electron energy loss spectroscopy offers a direct probe of the interband transitions in semiconductors and therefore allows us to study the electronic structures of ZnO in a microscopic scale.[4] Our findings indicate the grain boundaries indeed act as optical reflectors, which facilitate the scattering of light.

Thin films of ZnO are deposited on amorphous fused quartz by pulsed laser deposition.[3] Experimental apparatus and procedure have been described previously.[5] Laser action has been observed in polycrystalline films at the ultraviolet (UV) region of 3.20 eV ($\sim$388 nm). TEM and EELS measurements are acquired by using a Hitachi H2000 analytical transmission microscope, operated at an accelerating voltage of 200 keV. The microscope is equipped with a cold-field emission gun with an energy resolution of 0.5 eV determined by the full width at half maximum (FWHM) of the zero loss peak. It is also installed with an Oxford Pentafet x-ray detector and a Gatan-666 transmission EEL spectrometer. The electron beam is focused to give a beam diameter of less than 2 nm. The EELS measurements are carried out with the irradiated area identical to the profile of the electron beam. Low energy valence excitation loss spectra (-10–50 eV) are collected at the grains and grain boundaries. The conversion of energy loss spectra to dielectric functions is carried out by following the procedures given in the published

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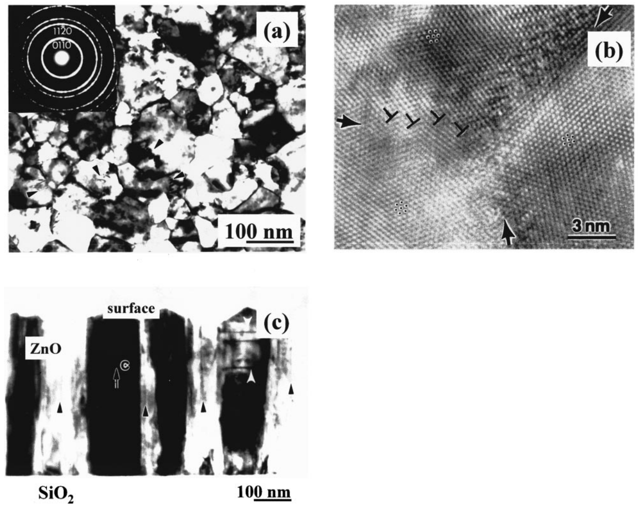

FIG. 1. The TEM images of polycrystalline ZnO films. The plan-view image together with the electron diffraction pattern (EDP) (a) shows the irregular shape of the microcrystallities. The grain size measured is typically smaller than 100 nm. High-resolution plan-view image in (b) shows that the grain boundaries, indicated by arrows, jointed by three crystallities. Threading dislocations can be easily seen at the boundaries. Hexagonal dots indicate wurtzite structure. A crosssection TEM image (c) is shown to illustrate the columnar growth mode of the film. Arrows indicate the position of defects.

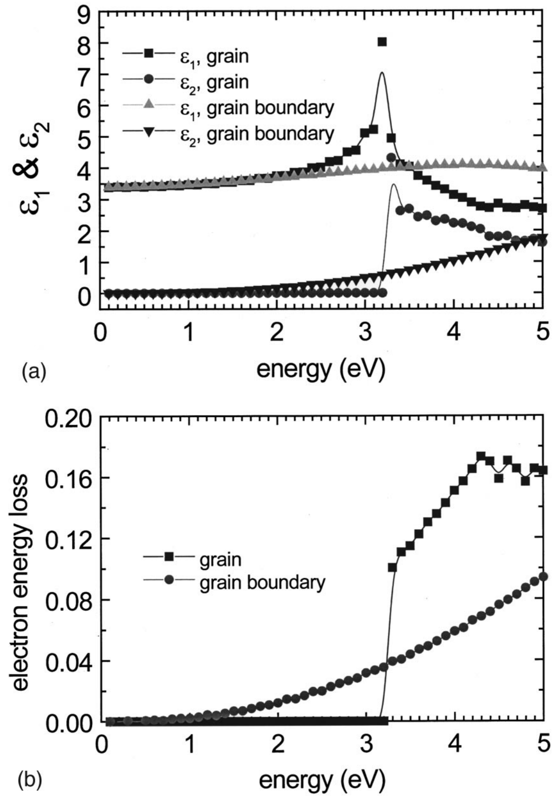

FIG. 2. The complex dielectric functions of the grain and grain boundaries (a) of ZnO films. The filled squares and circles represent the real and imaginary parts of the dielectric function of the grains and the filled triangles and inverted triangles represent the real and imaginary parts of the dielectric function of the grain boundaries. The corresponding loss functions (b) are also illustrated.

literature.[4,6] These include the single-scattering deconvolution of removing the zero loss peak using Lorentizian peak fit, convergence and angular correction, and Kramers-Kronig analysis.[4,6] All the measurements are performed at room temperature.

X-ray $\theta/2\theta$ analysis indicates ZnO films are textured in c-axis orientation with respect to the substrate normal, and the (FWHM) of (0002) ω-rocking curve is shown to have a mosaic spread of $0.9°-1°$. In-plane Φ scans of the films exhibit no peak-like features confirming the fact that amorphous substrate does not support any epitaxial growth.

TEM analysis shows the ZnO polycrystalline film consists of a highly disordered structure. Figure 1(a) show a plane-view TEM image of ZnO film together with an electron diffraction pattern (EDP). The polycrystalline grain structure of ZnO is quite evident in the TEM image. The different contrast of the grains shows there exists certain misorientation of individual grains with respect to the c axis. The grains appear in irregular shapes with their sizes ranging from 50 to 150 nm. Consistent with the results of XRD, EDP shows a series of diffraction ring pattern confirming the absence of any preferential in-plane orientation. High-resolution plain-view image in Fig. 1(b) shows that the grain boundaries are almost atomically sharp and are believed to consist of various defects such as dislocations and distorted tetrahedra. A cross-section TEM image is shown in Fig. 1(c) to illustrate the columnar growth mode of the film. The grain boundaries are clearly visible between adjacent columnar grains and normal to the substrate plane implying no coalescence of ZnO nuclei takes place after a few monolayers. The interface between the film and substrate is relatively flat. Within individual grains, the defect structure is rather similar to that of published results for the epitaxial ZnO thin films.[7] The threading dislocation density is found to decrease as a function of thickness, from 10^{12} at the interface to $10^{9}\,cm^{-2}$ at the surface. The dislocations are also found to lie in the basal plane, which is opposite to that of nitride-based semiconductors. Stacking faults and inversion domains are frequently observed at the film bulk and interface. Energy dispersive x-ray (EDX) analysis of the film shows only Zn and O suggesting no Si diffuses from substrate to the bulk of the film to form $ZnSiO_4$. As a result, high resolution TEM illustrate the structures of our ZnO films, even within the grains, are far less than the device quality of GaAs and ZnSe based materials. Hence, the realization of excitonic emissions[8–10] and laser action[3,8,9] in ZnO assumes that the optical properties of this material in fact has a very high tolerance on structural defects and deserves further attention.

To elucidate the mechanism of light scattering in ZnO, the electronic structures of the grain and grain boundary have been studied by EELS. Figure 2 illustrates the complex dielectric functions of ZnO grain over the spectral range of 1 and 5 eV transformed from the EEL function using Kramers–Kronig analysis. A strong and well-defined excitonic peak is exhibited at ~ 3.32 eV and is consistent with the results of Washington *et al.*[5] and Jellison and Boatner.[11] However, the magnitudes of the our dielectric functions at the excitonic resonance region, 3–3.5 eV for ε_1 and 3.2–3.7 eV for ε_2, are closer to that of Jellison and Boaterner than that of Washington *et al.* due to the uncorrected pseudo functions in the latter one. The dielectric functions of the grain at photon energy extended from 5 to 50 eV are found to be compatible to that of single-crystalline ZnO.[12] The dielectric

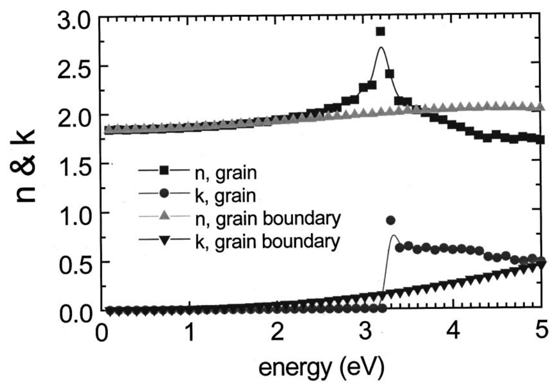

FIG. 3. The refractive indexes and extinction coefficients of the grain and grain boundaries of ZnO films.

functions of the grain boundary are also shown in Fig. 2. An absence of the excitonic feature in the grain boundary spectra is clearly observed. The lack of excitonic transitions in the grain boundary can be understood by realizing that the grain boundaries are usually very structural defective.[1,2] The defects act as nonradiative recombination centers, which decompose excitons.[1,2] When excitons recombine in the vicinity of defects, the energy released tends to heat up the crystal instead of producing light.

Figure 3 illustrates the refractive indexes (n) and extinction coefficients (k) of the grain and grain boundary computed from the corresponding dielectric functions. It is obvious that the refractive index of the grain boundary is significantly lower than that of the grain due to the lack of excitonic resonance. When light propagates from one medium to another with lower refractive index, it experiences internal reflections dependent on the angle of incidence.[13] The exact scenario can apply to our situation where multiple internal reflection or scattering indeed occurs in the disordered medium of the nonepitaxial ZnO films and supports the argument that the self-formation of laser cavities is caused by the strong scattering of light. However, due to the fact that the thickness of the grain boundaries approaches to the monolayer level, some photons may be energetic enough to travel for a very long distance after the emissions but eventually will be trapped. This also explains the fact that the size of the laser cavities increases as a function of pump light intensity.[3] The size and shape of the cavities are determined by many factors. However, we have estimated the reflectivity of the grain boundary system at a normal incidence.[13] This will set the upper bound value of the reflectivity as a function of incidence angle. Assuming the optical constants, n and k, of the grain and grain boundary to be 2.6 and 0.4 and 1.9 and 0.15, respectively, the reflectivity at the lasing wavelength of 388 nm is deduced to be 0.0005–0.0018 if the thickness of the grain boundary varies from 20 to 40 Å.[13] It is also noted that the lasing emissions occur at the wavelength where the refractive index mismatch is the largest between the grain and grain boundary. This implies that the strong optical scattering will more or less navigate the lasing emissions.

In short, the structural and electronic properties of polycrystalline ZnO thin films grown on amorphous fused quartz have been studied by TEM and EELS. Results have shown that the refractive index of the grain boundary is significantly lower than that of the grain due to the lack of excitonic transitions. This observation substantiates the formation of self-assemble laser cavities in ZnO films is caused by the strong optical scattering occurred at the grain boundaries. In addition, our results also imply the criteria of the formation of laser cavities which involve two intrinsic factors of the material: strong excitonic character and high defect tolerance.

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