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Optical characteristics of ZnO single crystal grown by the hydrothermal method

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ABSTRACT

ZnO single crystals have been grown by the hydrothermal method. Raman scattering and Photoluminescence spectroscopy (PL) have been used to study samples of ZnO that were unannealed or annealed in different ambient gases. It is suggested that the green emission may originate from defects related to copper in our samples.

KEYWORDS

Hydrothermal growth;
Photoluminescence.

INTRODUCTION

Among wide-band-gap semiconductors ZnO is one of the promising materials for the fabrication of UV and visible light emitting devices, which recently attracted particular attention due to its remarkable optical properties[1-3]. Research in ZnO has recently been proceeding at a rapid pace, due largely to advances in bulk and epitaxial growth methodology[4,5]. Although most thinfilm growth at the present time is on lattice-mismatched substrates, such as Al_2O_3 or Si, the demands for higher quality material are requiring the development of large-area ZnO substrates to facilitate homoepitaxial growth. Two-inch wafers grown from the vapor phase have been commercially available for several years now[6]. But more recently the melt and hydrothermal methods have been successfully used to grow two-inch, and even larger crystals[7]. However, there still remain serious problems with bulk-ZnO crystals. The broad peak emission from a deep level at 2.2 eV-2.4 eV, called the green band, is problematic in ZnO-based devices[8–11]. However, the origin of the green emission is still controversial. Various models include the involvement of oxygen vacancies[12,13], interstitial O[14,15], Zn vacancies, and Zn interstitials[16], or even substitutional Cu[17]. Nevertheless, the exact mechanism responsible for the green PL is still not clearly understood. As a result, further experimental and theoretical investigation is required to understand the optical properties of bulk ZnO.

In this paper, we investigate the growth of ZnO single crystals grown by the hydrothermal method. The crystals were processed under several annealing conditions and were characterized by photoluminescence spectroscopy (PL) and Raman scattering at room temperature. The origin of a green emission in undoped ZnO is discussed.

EXPERIMENTAL SECTION

ZnO single crystals were grown in an autoclave, which was made of high-strength steel. The nutrition chamber contained solid nutrients and the growing chamber contained several ZnO seed crystals. The nutrients were prepared from 99.99% ZnO powder, which was sintered for 30 h in air at 1200 ! in a platinum crucible. The seed crystals were (0001) plates, which were cut from a commercial ZnO crystal grown using the chemical vapor transport (CVT) method, and were suspended by Au wires on an Au ladder. The seed crystals and the nutrient were separated by a baffle. Further details about the apparatus are described elsewhere[18]. The mineralizer solution poured into the gold liner was a mixture of KOH (3.0mol/l), LiOH (1.0mol/l) and H_2O_2 (1wt %) with a filling grade of 75%. Suitable quantity of distilled water was supplied into the volume between the autoclave and the Au liner for pressure balancing. During the growth process, the nutrition chamber was kept at 350-370 ! with a temperature gradient of 10–15 ! declining towards the growth chamber, so as to create a convection current for the transportation of dissolved nutrients to the crystal seeds located in the lower temperature chamber. The pressure was about 1200 atm, which was measured by a pressure gauge. The temperature of the seed region was set at about 15~20 ! lower than that of the nutrient region. After 20~30 days, the autoclave was cooled down and bulk crystals were withdrawn.

The wafers were sliced from the zinc atom terminated face (+c surface), and the oxygen atom terminated face (-c surface) of the bulk ZnO single crystal, for further investigation. A series of samples were prepared by annealing in air ambient at temperatures ranging from 400 ! to 1200 !, and some of the samples were annealed in H_2 ambient at 600 ! for 2 hours. The Raman spectra were recorded at room temperature by using a Jobin Yvon LabRAM spectrometer and a charge-coupled device CCD camera with a resolution of 1 cm$^{”1}$ per pixel. PL measurements were carried out using a Xe arc lamp light at room temperature. Raman scattering was supplied by a JYT 4000 at room temperature.

RESULTS AND DISCUSSION

The Raman back scattering results of the as-grown and annealed ZnO single crystal samples are shown in Figure 1 (532 nm, for VV polarization, VV refers to the scattering configuration). As shown in the figure, there are four peaks, occurring at wave numbers 118, 327, 437 and 1147 cm^{-1} in the spectrum of the as-grown ZnO crystal. According to the selection rule of the phonon mode in ZnO, the predominant peak at 437 cm^{-1} is the high frequency E_2 phonon characteristic of the wurtzite structure. The 327 cm^{-1} mode corresponds to the second order phonon $2E_2$ (TO) of the low-frequency phonon (at 160 cm^{-1})[19]. The 1147 cm^{-1} peak is assigned to the $2E_{1L}$ phonon. It is generally accepted that the appearance of well-resolved Raman peaks is related to multiphonon and resonance processes, and the absence of a E_1 (LO) peak at 588 cm^{-1} is related to oxygen deficiencies[20]. After high-temperature annealing, the optical quality of the crystal is further improved. This improvement is reflected in figure 1, which the intensity of the 437 cm^{-1} (E_2 mode) peak increases a little after annealing. Such an increase in the intensity of the Raman peak indicates that the growth-induce strain is reduced, and thus the crystalline quality improves after annealing. Generally, the nonpolar E_2 modes appear in the unpolarized Raman spectra of bulk ZnO crystals under back-scattering geometry. After electron irradiation, a broad peak at 575 cm^{-1} will appear. The A_1 575 cm^{-1} is the A_1 (LO) mode and is associated with oxygen vacancy defects (O_V) or complexes[21]. This mode is mostly observed in electron irradiated ZnO single crystals[22].

Room temperature PL results of air annealed ZnO wafers excited by a Xe arc lamp at 300 nm, are shown in Figure 2. The wafers excited by the Xe arc lamp

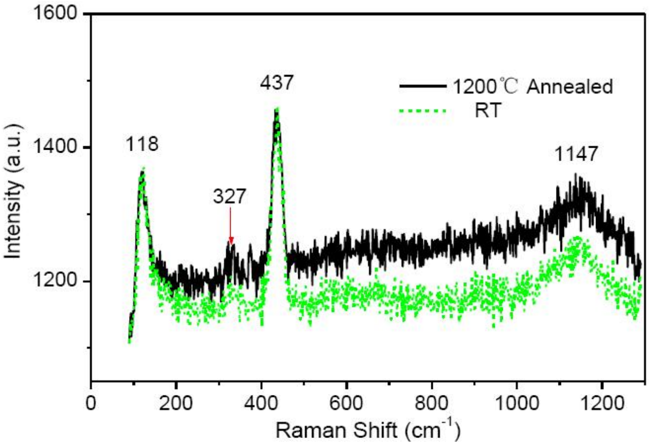

Figure 1 : Room temperature Raman scattering spectra of as-grown and annealed in oxygen ambient ZnO crystals.

have strong UV emission and green emission, while the wafers excited by the synchrotron radiation exhibit very strong, broad green-light emission and weak UV emission. For the 331 nm emission, we suggest it is due to the up-shift of the band edge emission because the energy interval between 331 nm and 376 nm (band edge emission) is 0.449 eV, just corresponding to the energy of the OH-strech local vibration mode (3616.3 cm^{-1}, 0.449 eV). Actually, hydrogen atoms are known to be easily incorporated into hydrothermally grown crystals[23], and the most stable form of hydrogen and host atoms is in the bond-centered configuration[24], where the OH-vibration energy is 3616.3 cm^{-1}. The enhanced emission at 331nm of the hydrogen annealed wafer also supports the above supposition, which we will discuss below in the next section. The green-peak near 540 nm is a widely observed defect related emission in ZnO and various papers in the literature attribute a green luminescence emission in ZnO to a diverse set of mechanisms. Many of the explanations are based on a minimum of evidence. We have shown conclusively that one type of green emission is due to copper impurities present at levels much less than 1 ppm in the crystals[25]. The assignment of a second green band has not clearly been established. One possible model is donor-acceptor pair recombination where the acceptor is Cu$^+$ and the donors are Group III impurities[25]. A second model is donor-acceptor pair recombination where the donor is an oxygen vacancy (acceptor unspecified or thought to be a zinc vacancy). A third model is an intracenter transition of a neutral oxygen vacancy (i.e., an S = 1 system)[26].

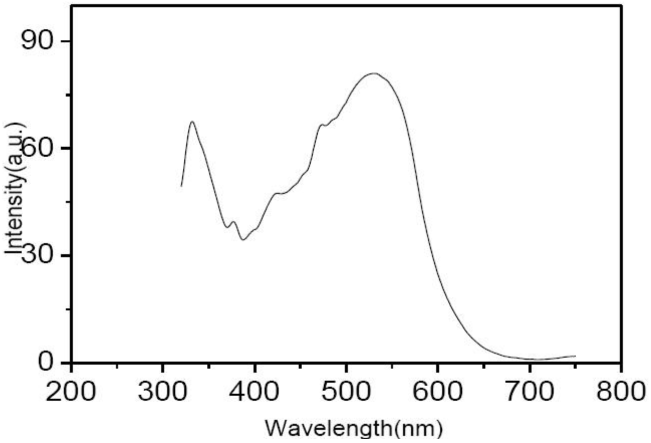

Figure 2 : Photoluminescence spectra from an undoped ZnO crystal taken after a thermal anneal at 1200 °C in air for several hours.

The PL spectra of hydrogen annealed ZnO wafers are depicted in Figure 3. Comparing the PL spectra obtained in Figure 2 and Figure 3, we can see that H_2 annealing decreases the intensity of the visible emission, and increases the ratio of emission intensity of the UV band and the green band. The 331 nm emission increased because the hydrogen atoms diffuse into the ZnO wafer, which is consistent with the above assumption that the 331 nm emission is related to the OH-stretch local vibration mode. Another feature also shown in Figure 3 is that the visible emission, especially the green emission is markedly passivated by the hydrogen annealing process. Furthermore, the result reveals that annealing in hydrogen ambient at an appropriate temperature would be an effective method to passivate visible emission in ZnO UV applications.

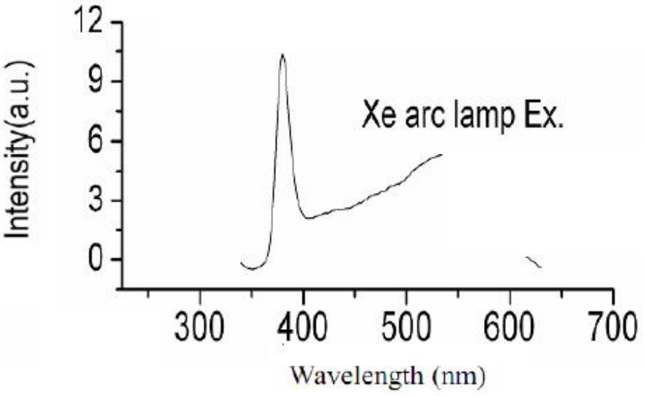

Figure 3 : PL spectra of hydrogen annealed ZnO wafers.

We display a logarithm plot of PL spectra at room temperature for ZnO wafers annealed air ambient at different temperatures, as shown in the left part of Figure 4. The ratio of integrated emission intensity of UV and green band light (the right part of Figure 4) decreases as the annealing temperature increases, which indicates that the annealing process causes the green emission increase. This phenomenon was also found in ZnO obtained by other techniques, they attribute the green emission to the defects in the band gap caused by distortions in the crystalline structure[27]. However, our sample was an undoped high quality crystal grown by the hydrothermal method. In addition to shallow donor impurities, the crystal contained trace amounts of copper ions. The green emission may originate from defects related to Cu ions in our samples. That correlation is certified by N. Y. Garces[25]. Holding the as-grown ZnO crystal for several hours at 1200°C in air changed the stable charge state of the Cu impurities from Cu^+ to Cu^{2+}, and conversely for hydrogen annealed ZnO wafers. The emission from the hydrogen annealed sample (with Cu^+ present) is unstructured (Figure 3), while the emission from the thermally annealed in air sample (with Cu^{2+} present) has the characteristic structure (Figure 2). Our data reaffirm that the green mission in ZnO is associated with Cu ions.

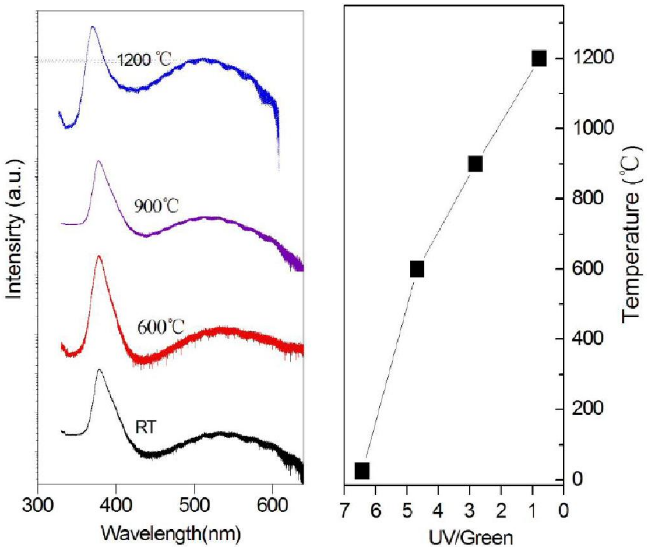

Figure 4 : A logarithmic plot of PL spectra for ZnO wafers annealed in air at different temperatures (left part) and the ratio of emission intensity of UV band and green band.

For the origin of the green emission, many mechanisms have been proposed and the widely accepted mechanism is singly ionized oxygen vacancy proposed by K.Vanheusden et al.[28]. They concluded that the green PL originates from a transition between singly charged oxygen vacancies and photoexcited holes because they observed a correlation between the intensities of the g=1.96 electron paramagnetic resonance (EPR) peak and the green PL. However, this correlation must be questioned because several of these investigators have mistakenly assigned the EPR signal at g=1.96 to singly ionized oxygen vacancies. The commonly observed EPR signal at g=1.96 is due to neutral shallow donors[29].

It should be noted that the EPR signal of Cu ions will appear on the high field side, which is not fall under our spectrum region. However, Dingle[17] has described a detailed study of a broad structured green emission band peaking in ZnO and concluded that it must be due to copper impurities. He showed that the zero-phonon line associated with this emission is split because of the two isotopes of copper (^{63}Cu and ^{65}Cu) and he also showed that the Zeeman splitting of these no-phonon emissions gave g values in direct agreement with the EPR results reported in Ref[25] for Cu in ZnO crystal.

CONCLUSION

In summary, ZnO single crystals have been grown by the hydrothermal method. In the photoluminescence spectrum, the UV band peaked at 331nm and green band emissions were observed under synchrotron and Xe arc lamp excitation. To determine the source of themÿthe PL of ZnO wafers unannealed and annealed in different ambient gases are further studied. The results from the present investigation suggest that the 331nm emission is due to the up-shift of the band edge emission, and the green emission may originate from defects related to the copper in our sample. The green emission can be passivated by the hydrogen annealing process. At the same time, the result reveals that annealing in hydrogen ambient at an appropriate temperature would be an effective method to passivate visible emission in ZnO UV applications. The effect of annealing temperature and annealing time in hydrogen ambient on visible emission in ZnO will be investigated in the next phase work.

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