Flux-Bridgman growth and characterization of Mn-doped ZnO single crystals

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Received 15 July 2011; Accepted 10 September 2011

Abstract: Mn-doped ZnO single crystals have been grown by the flux-Bridgman method from a high temperature solution of 24% ZnO-76% PbF$_2$ (molar fraction). A fast nucleation was induced by the gas-cooling system at the bottom of the Pt crucible. A red Mn:ZnO crystal up to 13 mm×15 mm×(3−4) mm was obtained. Powder XRD patterns showed that the as-grown crystals were in wurtzite structure. Electron Probe Microanalyser (EPMA) revealed that some PbF$_2$ inclusions formed due to fast nucleation. The additional Raman mode at 524 cm$^{-1}$ was attributed to the incorporation of Mn ions into ZnO crystal. Six-line hyperfine structure was observed in the electron paramagnetic resonance (EPR) spectra, which confirmed that Mn ions occupied Zn$^{2+}$ lattice sites with valence state of +2.

Key words: crystal growth; flux-Bridgman technique; Mn-doping; ZnO crystal

1 Introduction

ZnO normally has a wurtzite structure (space group P6$_3$mc) with lattice parameters $a$=0.325 3 nm and $c$=0.520 7 nm. Owing to its various excellent properties, ZnO is found to have applications in quite a few fields involving transparent conductors, gas sensors, varistors, surface acoustic wave devices and piezoelectric transducers [1]. In addition, ZnO is a direct wide band gap semiconductor with a large exciton bonding energy of 60 meV. So, it is a promising candidate for ultraviolet laser source and ultraviolet detectors [2]. Furthermore, some theoretical works on ferromagnetism of doped ZnO semiconductor have been published [3, 4]. ZnO crystals are expected to be a diluted magnetic semiconductor (DMS) above room temperature when doped with 3d transition metal (TM) atoms of Cr, Fe, V, Co, Mn. Among the researches focusing on the TM-doped ZnO semiconductors, more attention has been drawn on Mn- and Co-doped ZnO. However, compared with intensive reports on the preparation and properties of TM-doped ZnO films, powders, and nanoparticles [5−8], there are fewer studies concerning bulk TM-doped ZnO single crystals, mainly due to the difficulties in crystal growth.

It was reported that Mn-doped ZnO single crystal obtained by high pressure melt growth technique and Sn, Mn co-doped ZnO crystals by implanting method were reported with different magnetic characteristics [9−10]. MILLOT et al [11] presented the results of the investigation of structural and magnetic properties of Co-doped ZnO single crystals grown by chemical vapor transport (CVT). Although the preparation of Mn-doped ZnO films has been investigated in many cases, there are less detailed reports on the growth of Mn-doped ZnO bulk crystals. So far, ZnO crystals have been grown by the hydrothermal method [12], the flux method [13], the vertical Bridgman method [14] and the chemical vapor transport (CVT) method [15]. However, the growth of Mn:ZnO crystals is very difficult due to the polar growth of ZnO and the large ion radius of Mn$^{2+}$. Recently, we developed a flux Bridgman growth technique [16−19] and pure ZnO bulk crystals have been grown successfully from the high temperature solution of ZnO-PbF$_2$ system [20, 21]. In this work, the growth results and characterization of Mn-doped ZnO single crystals were reported.

2 Experimental

According to a previous work [21], the initial composition for ZnO crystal growth was optimized as
about 24% ZnO and 76% PbF₂ (molar fraction). In this experiment, the raw materials of ZnO and PbF₂ were weighed at the molar ratio of 24:76 and 2% (molar fraction) MnO₂ was added. They were loaded and sealed in a Pt crucible and fixed in a refractory tube. The crystal growth was carried out in a modified vertical Bridgman furnace with a gas-cooling system assembled at the crucible bottom. The growth temperature was controlled at 1 100 °C. When a stable temperature profile formed, O₂ gas flow was piped into the crucible bottom at an optimized rate of 3.0 L/min. After the growth finished, Mn-doped ZnO crystals were separated mechanically from the solidified flux.

The as-grown crystal showed a 〈001〉 preferred orientation which was confirmed by the X-ray orientation. A small part of as-grown Mn:ZnO crystal was cut and ground into fine powders. Powder X-ray diffraction (XRD) was performed ranging from 10° to 80° (2θ). The compositions of as-grown crystal were characterized by EPMA and Mn content in the crystal was determined by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Raman scattering spectrum was measured on a JY LabRam-HR Raman spectrometer at room temperature with a backscattering configuration. A 325nm He-Cd laser was used as an excitation source. The EPR (electron paramagnetic resonance) experiments were performed at X band (9.066 GHz) on a JEOL JES-FA200 ESR spectrometer.

3 Results and discussion

3.1 Crystal growth

It is difficult to grow ZnO crystal directly from its melt because of its strong volatility. For the growth of Mn:ZnO crystal, more difficulties come from the polar growth and the large ion radius of Mn²⁺. By considering that pure ZnO crystal has been grown from high temperature solution of ZnO-PbF₂, the flux Bridgman method provides a feasibility to grow Mn:ZnO crystal.

Lack of seed crystals, we designed a gas-cooling system at the crucible bottom to induce a single nucleus during the initial growth stage. When a stable temperature profile formed, the O₂ gas flow was introduced, which resulted in a sudden drop of the temperature at the center of the crucible bottom. Therefore, the supersaturation was achieved to form a fast induced nucleus at the center bottom of the crucible. Then, Mn:ZnO crystal grew up based on the nucleus with the lowering of the crucible. Figure 1 shows the curve of temperature drop vs time at a gas rate of 3 L/min. In the first 15 min, the temperature declined rapidly by nearly 15 °C, and in the next two 30 min the temperature dropped by 10 °C and 5 °C, respectively, then it reached a stable solid/liquid interface again. The growth parameters were optimized as follows: O₂ gas flow rate was about 3 L/min; the lowering rate was 0.3 mm/h.

In order to obtain a large crystal, the nucleation was a key issue for successful growth of Mn:ZnO crystals. Figure 2 shows the nucleation core at the bottom of the ingot obtained in this experiment. It showed the distinct change of color from the nucleation area to the outside of the ingot, which mainly came from a covering layer of the solidified flux. When the crystal was separated from the flux, a transparent material with a diameter of about 13~15 mm and a thickness of 3~5 mm was obtained. The center part (about d 5 mm) was slightly darker than the outside of the crystal, as shown in Fig. 3. In our previous works [20, 21], pure ZnO crystals have been grown by the same process and the pure ZnO crystals showed tawny color. We may conclude that the red color comes from the incorporation of Mn ions into the crystal.
3.2 Crystal structure

A small sample was cut from the transparent crystal and was ground into fine powders for XRD and ICP measurements. The powder XRD data showed that the crystal and the 4N-ZnO powder were of the same wurtzite structure as depicted in Fig. 4. The calculated lattice parameters of as-grown crystal were \( a = 3.249 \) Å and \( c = 5.207 \) Å, which were slightly larger than those of 4N-ZnO powders (\( a = 3.243 \) Å and \( c = 5.198 \) Å). It is consistent with the fact that Mn\(^{2+}\) has larger ionic radius than Zn\(^{2+}\). Additionally, we observed three weak peaks in the XRD patterns, which were attributed to the existence of PbF\(_2\) phase. As mentioned above, the nucleus was formed by sudden gas-cooling process and some PbF\(_2\) fluxes were inevitably frozen in the Mn-doped ZnO crystal.

3.3 Microarea composition analysis

Figure 5 shows the typical morphology of the unpolished Mn-doped ZnO crystal surface. There are some white dots in the matrix. Their compositions were checked by means of microarea composition analysis. The results are listed in Table 1. The main composition of matrix was ZnO and the white dots were determined as PbF\(_2\) with some amounts of ZnF\(_2\). ICP-AES was performed to test the content of Mn dopant. The result gave a value of 0.093\% (molar fraction) Mn in as-grown ZnO crystal, which was much less than that of the initial composition. This result was reasonable for the following considerations. Firstly, ZnO has a strong polarity and the oppositely charged ions produce positively charged Zn (001) and negatively charged O (00\(\bar{1}\)) surface. Mn\(^{2+}\) has larger ionic radius than Zn\(^{2+}\) and is difficult to enter into the lattice. Secondly, the considerable segregation of MnO\(_2\) in the PbF\(_2\)-ZnO binary results in low content of Mn\(^{2+}\) in as-grown crystal.

3.4 Raman spectra

Raman scattering was used to study the effect of manganese doping on ZnO vibration modes. Figure 6 shows the Raman spectrum of Mn-doped ZnO crystal measured at room temperature. Four vibration modes were observed at 99, 331, 437 and 524 cm\(^{-1}\) and a band at 572 cm\(^{-1}\). The three phonon modes at 99, 437 and 524 cm\(^{-1}\) are ascribed to \( E_2 \) (low), \( E_2 \) (high) and \( A_1 \) (LO), respectively. The phonon mode at 331 cm\(^{-1}\) is assigned to a second-order phonon originated from the zone-boundary phonons of \( E_2 \) low-frequency branch [22]. Several researchers have reported the peak at about 522 cm\(^{-1}\) in Mn-doped ZnO films and powders [23–25]. The detailed discussion on Mn:ZnO crystal has been reported.
Therefore, the additional Raman peak at 524 cm$^{-1}$ originated from the incorporation of Mn ions into wurtzite ZnO crystal.

Fig. 6 Raman spectrum of Mn-doped ZnO crystal measured at room temperature

3.5 EPR Measurement

EPR measurements were conducted to get the information about the valence state and site occupancy of the Mn ions in the host crystal lattice. The Mn$^{2+}$ has an electronic configuration of 3d$^5$ with spin $S=5/2$ and angular momentum $L=0$. And the 100% abundant isotope is $^{55}\text{Mn}$, which has nucleus spin $I=5/2$. The resonance of an isolated Mn$^{2+}$ ion located substitutionally on a Zn lattice site in hexagonal ZnO is described by the spin Hamiltonian:

$$\begin{align*}
H &= g\beta H \cdot S + \frac{1}{6}a(S_z^4 + S_y^4 + S_x^4) + \\
&+ D\left(S_z^2 - \frac{1}{3}(S(S+1))\right) + AS \cdot I
\end{align*}$$

where the first term describes the Zeeman interaction, the two following terms corresponds to the axial zero-field splitting. The last one accounts for the hyperfine structure term.

In order to distinguish the anisotropic contribution of axial fine structure splitting, Mn-doped ZnO single crystal was ground into powder sample for measurement. The room-temperature EPR spectra of Mn-doped ZnO powders are shown in Fig. 7. Sweep time for sample (a) was 1 min, while it was 4 min for samples (b) and (c). And samples (b) and (c) were measured under parallel and perpendicular magnetic fields, respectively. No difference was shown between the spectra of samples (b) and (c), which reflected the isotropy of the powder samples. A six line spectrum with a hyperfine splitting of about 7.8 mT (72.7 × 10$^{-4}$ cm$^{-1}$) was observed on all the three spectra. The most intense hyperfine lines were found for the central transition, $M_S=+1/2 \leftrightarrow -1/2$. From the EPR spectra, we determined the Landé g factor in the Zeeman interaction term to be 1.998. This spectrum with characteristic sextet hyperfine structure has been observed in Mn-doped ZnO nanocrystals and films [27–29], which was attributed to isolated Mn$^{2+}$ substitutionally on Zn$^{2+}$ sites. As for exchange-coupled Mn$^{2+}$ ions, the dipolar interactions produce broad EPR signals rather than six-line splitting. So, the EPR spectra validated that Mn ions incorporated into the crystal with a valence state of +2 and isolated from each other.

Fig. 7 EPR spectra of Mn-doped ZnO single crystal at room temperature: (a) Sweep time 1 min; (b) Sweep time 4 min, under parallel magnetic field; (c) Sweep time 4 min, under perpendicular magnetic field

4 Conclusions

The flux Bridgman growth of Mn-doped ZnO crystals has been investigated and a Mn:ZnO single crystal with a dimension of 13 mm × 15 mm × (3–4) mm has been obtained from the high temperature solution of 24% ZnO-76% PbF$_2$ (molar fraction). Electron probe revealed that some PbF$_2$ inclusions were found on the surface of ZnO crystals. The as-grown crystal was transparent with a red color, which suggested the Mn$^{2+}$ doping. The increase of the lattice parameters and the appearance of an additional Raman mode at 524 cm$^{-1}$ also confirmed the incorporation of Mn ions into ZnO crystal. The six-line hyperfine structure in EPR spectra revealed that the Mn$^{2+}$ occupied Zn$^{2+}$ lattice sites but no dipolar interaction existed within the Mn ions.

References


