Optical transitions and multiphonon Raman scattering of Cu doped ZnO and MgZnO ceramics

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Abstract: Cu doped ZnO and MgZnO ceramics were created via a process of cold pressing and annealing, and their optical properties and phonon dynamics were studied. It was found that the ceramics exhibit infrared absorption peak energies at 5783 and 5822 cm⁻¹, indicative of intraband transitions in a substitutitional Cu ion of oxidation state +2. The UV photoluminescence (PL) intensity of the ceramics was found to weaken significantly relative to an undoped sample. The low PL intensity is discussed in terms of the Cu/Zn1−xO alloy system and the indirect bandgap of the CuO end member, as well as in terms of the nonradiative Cu centers. Due to the weak PL, up to ten LO multiphonons were observed in the Raman spectra, pointing to a strong polaron coupling. The resonance behavior of the highest intensity mode was found to exhibit outgoing resonance characteristics. © 2009 American Institute of Physics. [DOI: 10.1063/1.3081628]

ZnO and MgZn1−xO have been identified as promising materials capable of efficient luminescence and absorption at the UV range of the spectrum. ZnO has a direct bandgap of ~3.4 eV and that of MgO is ~7.7 eV; thus, depending on their solubility limit, the resulting solid solution of the two oxides should yield materials of engineered bandgaps at the oxidation state +2. The UV photoluminescence (PL) intensity of the ceramics was found to weaken significantly relative to an undoped sample. The low PL intensity is discussed in terms of the Cu/Zn1−xO alloy system and the indirect bandgap of the CuO end member, as well as in terms of the nonradiative Cu centers. Due to the weak PL, up to ten LO multiphonons were observed in the Raman spectra, pointing to a strong polaron coupling. The resonance behavior of the highest intensity mode was found to exhibit outgoing resonance characteristics.

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attributed to intraband transitions in the substitutional Cu$^{2+}$ ion in ZnO that involve the $^7T_2$ and the $^2E$ states. The XPS studies concluded that the Cu ions in ZnO have binding energies 954 and 934 eV, corresponding to oxidation state +2. The above studies indicate that the Cu ions are incorporated as neutral acceptors in the Cu$_{0.0025}$Zn$_{0.9975}$O sample.

The PL spectra of the Cu doped ceramics were found to be very weak relative to an undoped ZnO ceramic sample. Figure 3 depicts the spectrum acquired at 77 K of the Cu$_{0.0025}$Zn$_{0.9975}$O ceramic. The absorption at 5783 and at 5822 cm$^{-1}$ are indicative of transitions between the states of a substitutional Cu$^{2+}$ ion.

The IR absorption spectra of the Cu$_{0.0025}$Zn$_{0.9975}$O ceramic sample. The absorptions at 5783 and at 5822 cm$^{-1}$ are indicative of transitions between the states of a substitutional Cu$^{2+}$ ion.

system that can impact the PL efficiency. However, the PL was found to diminish significantly at low Cu concentration ($\approx$ 0.0025) at which the bandgap is expected to retain its direct nature. A more plausible reason for the weak PL of the ceramics may be the nonradiative centers relating to the Cu dopants. First-principle calculations have indicated that Cu atoms have low substitutional formation energy in ZnO, and in conjunction with the high ionization energy of the Cu, deep in-gap states of high density can form. As a consequence, the Cu centers in ZnO can act as traps to the excited electrons, thus diminishing the PL efficiency. No material degradation due to the Cu incorporation that impacts the optical quality of the ceramics is evident. As can be inferred from the Raman scattering of these samples, the ceramics are of high optical quality. Raman scattering is an inherently weak effect in solids; however, in the ceramics up to approximately ten LO, peaks of significant Raman intensity can be observed even at room temperature.

The low PL intensity of the Cu$_{0.0025}$Zn$_{0.9975}$O ceramics enables the study of the LO multiphonon mode characteristics. In general, the number of LO phonons in semiconductors varies monotonically with the polaron coupling coefficient. The polaron coefficient is a measure of the strength of the electron-phonon interaction and determines the availability of relaxation paths and transport properties of the excited electrons in a semiconductor. The polaron coupling coefficient of ZnO has been previously reported to be $\approx$ 0.9; for comparison, InAs, which is a weaker polar semiconductor, has a polaron coupling of $\approx$ 0.02. As can be seen in Fig. 3, up to ten LO (10LO) phonon modes are observed in the Raman spectrum of the Cu$_{0.0025}$Zn$_{0.9975}$O ceramic. This is comparable to the value found previously for bulk ZnO.

In addition, it is evident from Fig. 3 that the maximum LO intensity is at 7LO, which coincides with the energy of the PL at 3.31 eV. This observation is consistent with an outgoing resonant behavior: $E_{\text{PL}} = nE_{\text{LO}} = E_{\text{crystal states}}$, i.e., the scattered energy is equal to some electronic states of the crystal. In our case, we found $n = 7$ and LO energy is 0.072 eV (corresponding to 582 cm$^{-1}$). Thus, the scattered energy of the 7LO for a laser excitation line 3.81 eV can be expressed as 3.81 − 7 × 0.072 $\approx$ 3.31 eV, which is equal to the PL energy as can be seen in the left inset to Fig. 3. Therefore the resonance process is coupled to the electronic states corresponding to those responsible for the PL transitions. In ZnO single crystal, the UV PL is of excitonic origin; however, recent reports have indicated that the UV PL of ZnO can be also due to recombination between defect states. We have previously found that in our ZnO and Mg$_{0.1}$Zn$_{0.9}$O nanocrystals synthesized via a thermal decomposition method, the dominant bandedge PL at the cold temperature regime is due to defectlike states, while at room temperature the excitonic transitions come into play. Future research will address the nature of the PL of the ceramics samples.

To gain further insight into the phonon dynamics of the ceramics, a Cu$_{0.05}$Mg$_{0.1}$Zn$_{0.85}$O sample was created. The rationale was to achieve a ceramic of a new bandgap and of a very weak PL, both features that should enable different conditions for the Raman properties than that investigated above for Cu$_{0.0025}$Zn$_{0.9975}$O. Figure 4 depicts the phonon spectrum...
PL energy of the Cu$_{0.0025}$Zn$_{0.9975}$O. Similar blueshift of the PL energy has been previously observed in MgZnO thin films and nanocrystals.\textsuperscript{1,7,12} Moreover, as can be seen in Fig. 4, the spectra exhibit nine LO multimodes. MgO is a stronger polar material than ZnO, and an increase in the multiphonon scatterings relative to that of Cu$_{0.05}$Mg$_{0.3}$Zn$_{0.65}$O is expected. However, the Raman lines of the Cu$_{0.05}$Mg$_{0.3}$Zn$_{0.65}$O are broad, which impedes the detection of the higher order LO multimodes in that sample. Broader Raman lineshapes are expected in an alloy system due to inhomogeneous distribution of the alloy constituents. With regard to the resonance characteristics, the 1LO mode of the Cu$_{0.05}$Mg$_{0.3}$Zn$_{0.65}$O sample is at LO=0.075 eV (corresponding to 606 cm$^{-1}$), and the maximum intensity occurs at n=3; therefore, the scattered energy of the 3LO is 3.81−3 ×0.075=3.58 eV, which is consistent with the energy of the PL at ~3.57 eV (see inset to Fig. 4). Similar to the Raman characteristics of Cu$_{0.0025}$Zn$_{0.9975}$O, the Raman of Cu$_{0.05}$Mg$_{0.3}$Zn$_{0.65}$O is consistent with an outgoing resonance. Outgoing LO resonance in MgZnO thin films grown via PLD have been previously studied, however it was found that for Mg$_{0.3}$Zn$_{0.65}$O film the LO frequency is at ~640 cm$^{-1}$\textsuperscript{24} for the Cu$_{0.05}$Mg$_{0.3}$Zn$_{0.65}$O ceramic, the LO is at 606 cm$^{-1}$ corresponding to a lower Mg composition in the alloy. We attribute this difference to MgO segregates at the grain boundaries of the ceramic sample. This form of MgO was detected via the XPS and the EDX but is not part of the alloy; thus, a lower phonon frequency is expected. Future research will address the exact behavior of the spatial compositional fluctuation of the ceramics.

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\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{(Color online) The Raman spectrum corrected for the PL background of the Cu$_{0.05}$Mg$_{0.3}$Zn$_{0.65}$O (in units of relative wavenumbers). The insets show the original spectrum, where the PL peak position is marked in units of eV. The spectrum was acquired at 77K. The 3LO has a resonance corresponding to the PL at ~3.57 eV.}
\end{figure}