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Research paper

# The saturable absorption and reverse saturable absorption properties of Cu doped zinc oxide thin films

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ABSTRACT

We present the structure and nonlinear absorption (NLA) properties of Cu-doped ZnO (CZO) films prepared by magnetron sputtering. The films were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The results show that the CZO films can maintain a wurtzite structure. Furthermore, the open-aperture (OA) Z-scan measurements of the film were carried out by nanosecond laser pulse. A transition from saturable absorption (SA) to reverse saturable absorption (RSA) was observed as the excitation intensity increasing. With good excellent nonlinear optical coefficient, the samples were expected to be the potential applications in optical devices.



## 1. Introduction

Zinc oxide (ZnO) has attracted the worldwide attentions because of its numerous applications in a variety of fields [1–4]. Many researchers have investigated the preparation and characterization of ZnO materials and various metal doped ZnO materials in recent years. For the later material, the different physical properties including band gap engineering (BGE) were modified [5]. It is well known that copper (Cu) is a luminescence activator in the II–VI group materials and, as expected, the Cu atoms can change emission by creating the localized energy levels inside the ZnO band gap, such as Cu acceptor with energy level ($E_c$ = −0.17 eV) below the conduction band [6,7]. By carefully controlling the doping content, Cu acts as one of the best elements for the BGE of ZnO. In addition, Cu is a prominent luminescence activator in II-VI compounds, as Cu dopant could modify the luminescence of ZnO crystal through creating localized impurity level [8]. Moreover, Cu has many similar physical and chemical properties compare to Zn. Cu doping has been reported to be able to change the microstructure and optical properties of ZnO thin films [8]. Recent papers on microstructure and different properties of Cu doped ZnO (CZO) materials have been reported, such as electrical [9,10], magnetic [11], ferromagnetism [12], piezooptical effects [13], photocatalytic performance [14] and photosensitivity properties [15]. The CZO materials can be synthesized by various technologies [16–21]. In principle, the dopants like Cu could be effectively used to addition control the density of the defect states, thereby tailoring the NLO characteristics. This result has not yet been reported.

In this letter, we firstly report the relation between defects and nonlinear optical characteristics in CZO thin films. The Z-scan is used to study the nonlinear optical properties of CZO film, which shows large nonlinear absorption coefficient and the changeover from saturable absorption to reverse saturable absorption for high excitation intensity. The experimental results provide the reliable reference for the application of CZO film in optical devices.

## 2. Materials and experiment

The CZO films were deposited on quartz substrates by simultaneous radio frequency MS of ZnO and direct current MS of Cu. The targets used in this study were sintered zinc oxide (99.99% purity, 60 mm diameter, 5 mm thickness) and metal Ag targets (99.99% purity, 60 mm diameter, 4 mm thickness). The substrate was ultrasonically cleaned in alcohol, and rinsed in deionized water. During deposition, the base pressure in the deposition chamber and radio frequency power were $6.0 \times 10^{-4}$ Pa and 100 W, respectively. Film growth was carried out in the growth ambient with the ratio of $O_2$ (reactive gas): Ar (sputtering gas) = 10:20 sccm at a constant working pressure of 1.0 Pa.

The crystal structure and morphology were studied by field emission scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The linear absorbance spectra and nonlin-

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ear optical characteristics spectrum were measured with a UV–vis-NIR Perkin-Elmer spectrophotometer and Z-scan technique [22,23], respectively. Those experimental techniques described in detail elsewhere [24].

## 3. Results and discussion

Fig. 1 shows the (002) diffraction peak for CZO films fabricated at different direct current power. As can be seen, all samples show the (002) diffraction peak characteristics of the ZnO. It shows that the preparation of the thin film sample c axis preferred orientation. As the direct current power increasing, the intensity of the (002) diffraction peak firstly increased and then decreased, reaching a maximum 4 W. This phenomenon happens due to that the moderate quantity of Cu atoms exists as interstitials, shares the oxygen with Zn atoms and hence improves the (002) orientation. However, the excess Cu-doping atoms can be energetically favorable to coalesce into metallic copper clusters and hence inhibit c-axis preferred growth of the ZnO film. Moreover, the intensity changing of peak characteristic for CZO can be attributed to the possible reasons: (1) the different radius of $Zn^{2+}$ and $Cu^{2+}$, and the electronegativity difference, result in the lattice distortion. In our experiment, the valence of Cu could be assumed to be +1 or/and +2 in the CZO films. The atomic radius of $Cu^{+}$, $Cu^{2+}$, and $Zn^{2+}$ are 0.096, 0.072, and 0.074 nm, respectively [25]. (2) The little amounts of Cu in the gaps between the lattices alter the fine structure of the crystal, which indicates that the CZO film fabricated at 4 W had the best crystal quality among all the CZO films. The average crystallite sizes of the samples were 16, 21, and 24 nm, respectively, as calculated using the Debye Scherrer equation ($0.9\lambda/B\cos\theta$) [26,27]. Thus, the substitution of $Cu^{+}$ for $Zn^{2+}$ ions increased as the direct current power increasing from 2 W to 8 W. When the direct current power exceeds 2 W and $Cu^{2+}$ substitution for $Zn^{2+}$ is predominant in the CZO film prepared at 2 W. Therefore, we can hypothesize that more $Cu^{+}$ ($Cu^{2+}$) substitution could occur in CZO film.

Fig. 2(a–d) shows representative SEM images of all samples. The image shows evidence of the nanostructured morphology of the pure ZnO (a) and CZO (b–d) film. It is evident that the grain size on the surface of pure ZnO film was not uniform. In Fig. 2a, the granulated morphology belongs to the (002) orientation, and the elongated ones belong to the (101) orientation. However, the CZO film exhibited a uniform grain size and a smooth surface, indicating good crystal quality. When the doping amount reached to a certain extent, the Cu is substituted on the Zn site, leading to the crystallization increasing of the thin film. The grain boundary resistance of ZnO increases one order of magnitude after the addition of a very small amount of Cu dopant. Due to the difference of ionic charge and radius between $Zn^{2+}$ and $Cu^{+}$, the segregation of Cu at the grain boundary of ZnO is preferred. Such segregation may establish a space charge zone near the grain boundary. Due to the presence of Cu dop ant in the lattice, the XRD–ZnO peaks decreased.

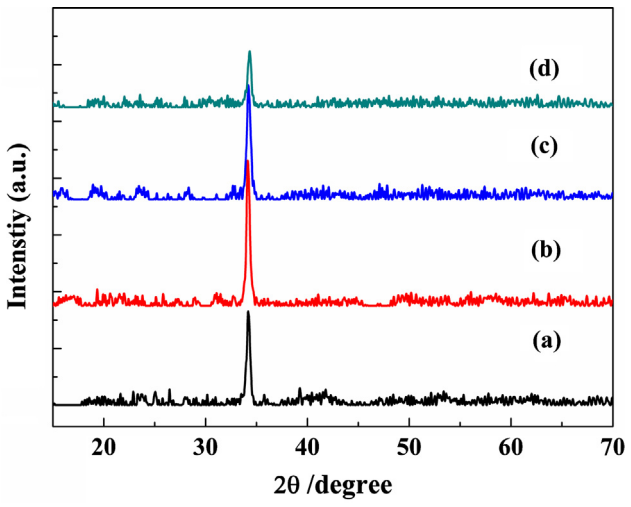


**Fig. 1.** XRD patterns of CZO thin films at direct current power of 2 W, 4 W, and 8 W, respectively.

The linear absorption (a) and transmission (b) spectrum of the all samples are shown in Fig. 3. According to the measured absorption spectra and using by the Tauc relationship [28], the band gap values of 3.22, 3.20 and 3.17 eV were obtained for CZO film at the direct current powers of 2 W, 4 W, and 8 W, respectively. It clearly indicates that Cu dopants are responsible to the intensity increasing of the band gap and red shift. The band gap of CZO decreased with the increasing of Cu concentration. Initial Cu doping is substituted on the Zn site, leading to the occurrence of sp-d spin exchange effect by transition metal localized delectronic and semiconductor band edge electronic.

To assess the behavior of the nonlinear absorption of the film as a function of input energy, the open aperture Z-scans were performed using nanosecond pulses for five different laser energies, namely 0.4 mJ, 0.6 mJ, 1.0 mJ, 1.4 mJ and 1.6 mJ, as shown in Fig. 4a–f. Because there are many types of mechanism can be used to explain the nonlinear optical properties, the contribution mainly depends on the duration time of the incident laser. When the duration of the incident laser is far less than the response time of a physical mechanism, the contribution to the nonlinear refractive index can be ignored. [29]. For the nanosecond laser, the pulse width is much less than the response time of thermal effect ($10^{-3}$–$10^{-4}$ s [29]) and the contributions of the thermal effect can be neglected. For the open-aperture case, the transmittance curve exhibits the peak and valley characteristic shape. A switch-over from saturable absorption (SA) to reverse-saturable absorption (RSA) is observed, as the energy of the laser beam increases from 0.4 mJ to 1.6 mJ. At lower input energies, Z-scan curve exhibits a peak at the focus, implying that SA plays a dominant role for the nonlinear optical properties. With the increasing of input laser energy, the peak disappears and a configuration of two peaks and a valley appear. This can be explained as follows: when the film is far away from the focus, the pump intensity is too low to induce nonlinearity and the transmittance is equal to unity. When the film is moved further near to the focus, the intensity of light falling on the sample increases and the ground state gets depleted causing absorption saturation, so that the transmittance increases. On the other hand, as the film reaches the focus, the high intensities are seen by the film. Meanwhile, the RSA dominates Hence transmittance decreases effectively and falls to a value less than unity. As the energy of laser beam continuing to increase (1.0 and 1.4 mJ), the valley depth is monotonically enhanced gradually as shown in Fig. 4. For higher energy (1.6 mJ), the nonlinear absorption overrides the ground state bleaching completely and shows deep valley indicating only RSA.

From the above-mentioned results, we can see two composite nonlinear absorptions with opposite signs in the CZO film at 532 nm. To interpret the flip of SA around the beam waist, we combine a SA coefficient and the two-photon absorption (TPA) coefficient, yielding the total absorption coefficient as [30]:

$$\alpha(I) = \alpha_0 \frac{1}{1 + I/I_s} + \beta I \tag{1}$$

where the first term describes negative nonlinear absorption such as SA and the second term describes positive nonlinear absorption such as RSA and/or TPA. $I$ and $I_s$ are laser radiation intensity and sat-