

Characterization of UV-modulated dielectric constant of ZnO thin films

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The modulation on complex dielectric constant of ZnO thin film with ultraviolet (UV) light is investigated by common-path heterodyne interferometer in visible range. The results indicate that the dielectric constant of ZnO thin film is reduced under UV irradiation. The dielectric constant recovers when the UV irradiation vanishes. As the dielectric constant is related to the charge density of bounded electrons, or so-called valence electrons, the influence of UV irradiation on the resistance of ZnO thin film was studied to clarify the physical mechanism associated with the UV-modulated dielectric constant. It was observed that a smaller resistance was achieved for ZnO thin film under UV irradiation. This implies that the valence electrons absorb the irradiated UV and become conduction electrons.

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1. Introduction

In recent years, ZnO has been widely applied in the electro-optical field due to versatility of energy band gap and refractive index. In the aspect of energy band gap, ZnO has a wide direct band gap (3.37 eV) and a large exciton binding energy (60 meV) [1]. The structure of three energy levels favorable for laser material has been developed for emitting devices like ultraviolet (UV) laser [2]. Furthermore, the optical band gap of ZnO film on fused quartz could be modulated from 3.13 to 4.06 eV by varying the growth temperatures [3]. This kind of controlling optical band gap by growth temperatures has successfully been applied for blue-light emitting diode [4]. Besides, the structure of energy level could also be verified by dopant concentration, and then the characteristic of photoluminescence emissions consequently ranges from green to yellow [5]. The featured phenomenon is applied to the phosphor of flat-panel displays of field emissive displays and cathodoluminescent devices [6].

The mentioned researches focus on manipulating the structure of the energy level/band gap for ZnO absorption/emitting. However, these optical properties are not suitable for visible band due to these energy gaps of Zinc oxide in UV band. Hence, ZnO thin film is viewed as transparent thin film for visible light and applied to one component of anti-reflection (AR) coating of solar cell. Besides, in the study on ZnO properties in visible band, the characteristic of refractive index dominates the propagation of visible light. And in manipulating refractive index, some researches indicate that refractive index of ZnO thin film is varied with preparation techniques or substrates [7-9]. However, to our knowledge, few studies focus on the modulation of refractive index by UV light. In this paper, we present the physical mechanism of the variation in refractive index of ZnO

with UV light, which could be applied to explain ZnO photoconductivity [10]. In the investigation of optical characteristics, the general instruments for the measurement of refractive index, like spectrometer [8] or ellipsometry [9], are not suitable for the measurement of optical characteristics variation induced by another modulation light, because in the detection process modulation light (e.g. UV light) mixes up easily with the studied light (e.g. visible light). Therefore the developed common-path heterodyne interferometer [11], based on the signal acquisition at the unique frequency occurred from the interference of two lights with same wavelength, is adopted to avoid the measurement error from stimulation, and then to identify the variation of refractive index/dielectric constant by UV light in this study. Similarly, in the electrical measurement, the used usual DC-measurements by the four-probe technique [9] are replaced by TFT-type pattern for the measurement of a tiny variation in the large electric resistance of thin film – mega-ohm for the investigated ZnO thin film – induced by UV illumination [12].

2. Experimental details

ZnO films are deposited on fused quartz substrate using a magnetron rf sputtering system with a sintered ZnO target (99.99%). At first, the sputtering chamber is evacuated to 2×10^{-3} Torr using a diffusion pump. Then the deposition of ZnO is carried out in a mixture of Ar (30%) and O₂ (70%) at the temperature of 200 °C. Consequently, measuring the geometry properties by optical profiler of Zygo Corp., the thickness of ZnO thin films and fused quartz are obtained at 6.532 μm and 2.051381 mm, separately, and their surface roughness are obtained at 522 nm and 6 nm, respectively. In order to

measure the complex refractive index of a ZnO thin film in the visible range, we use a home-made common-path heterodyne interferometer [11], as shown in Fig. 1.

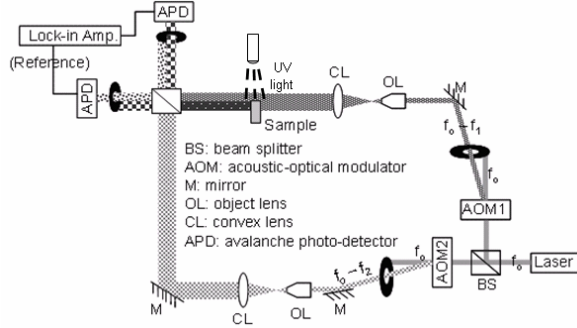


Fig.1. Scheme of home-made common-path heterodyne interferometer.

In this heterodyne interferometer, a parallel light of 532 nm in wavelength is emitted from a diode pump solid-state laser of Lasos Corp., and two acoustic-opto modulators (AOM) of Intra-Action Corp. are adopted to produce the heterodyne signal at the low frequency of 200 kHz for specification request of general optical detector and lock-in amplifier. To suppress the phase drift in the heterodyne signals due to vibration, air fluctuation, and temperature variation, the common-path technique is utilized in this interferometer. Thus, a high stability is achieved for the heterodyne signals. The details of the common-path heterodyne interferometer are given in [11]. The total complex transmission coefficient S_{21} of the ZnO/quartz system is measured using the interferometer. To obtain the complex dielectric constant $\epsilon_i = \epsilon_r + i\epsilon_i$ of the ZnO layer, we use the pre-measured complex refractive index of fused quartz ($\tilde{n} = 1.460 - i2.410 \times 10^{-8}$), its thickness ($d_2 = 2.051381$ mm) and its surface roughness ($z_2 = 6$ nm), the thickness of the ZnO layer ($d_1 = 6.532$ μ m), its surface roughness ($z_1 = 522$ nm) and the measured complex transmission coefficient S_{21} of ZnO/quartz. They are introduced in the complex transmission coefficient according to the generalized matrix method [13]:

$$S_{21} = e^{-i \frac{2\pi(\sqrt{\epsilon_1}d_1 + n_2d_2)}{\lambda}} \times \left\{ e^{i \frac{4\pi(\sqrt{\epsilon_1}d_1 + n_2d_2)}{\lambda}} - e^{-i \frac{8\pi^2(\epsilon_1 Z_a^2 + n_2^2 Z_b^2)}{\lambda^2}} \times \frac{(n_0 - \sqrt{\epsilon_1})(n_0 - n_2)}{(n_0 + n_2)(n_0 + n_2)} + e^{-i \frac{4\pi[-n_2d_2\lambda + 2\pi(n_0^2 Z_a^2 + \epsilon_1 Z_b^2)]}{\lambda^2}} \times \frac{(n_0 - \sqrt{\epsilon_1})(\sqrt{\epsilon_1} - n_2)}{(n_0 + \sqrt{\epsilon_1})(\sqrt{\epsilon_1} + n_2)} + e^{-i \frac{4\pi[-\sqrt{\epsilon_1}d_1\lambda + 2\pi(\epsilon_1 Z_b^2 + n_2^2 Z_a^2)]}{\lambda^2}} \times \frac{(\sqrt{\epsilon_1} - n_2)(n_2 - n_0)}{(n_0 + n_2)(\sqrt{\epsilon_1} + n_2)} \right\} \quad (1)$$

where, z , d , and n represent roughness, thickness, and refractive index, respectively. Subscript 0, 1, 2, a, and b are used to indicate parameters for air, ZnO film, quartz substrate, air-ZnO interface and substrate-air interface, in that order. From the obtained complex dielectric constant ϵ_i , the real part n_r and the imaginary part n_i of the refractive index of the ZnO thin film can be consequently found via

$$n_r = (\sqrt{\epsilon_r + i\epsilon_i} + \sqrt{\epsilon_r - i\epsilon_i})/2 \quad (2)$$

$$n_i = (\sqrt{\epsilon_r + i\epsilon_i} - \sqrt{\epsilon_r - i\epsilon_i})/2i \quad (3)$$

where the magnetic permeability of ZnO in visible band is treated as 1.

To investigate the modulation in the refractive index of a ZnO thin film by UV light, we irradiate the ZnO thin film by UV light given by a curving machine of Exfo Corp., with wavelengths ranging from 320 nm to 500 nm. The sample and irradiation direction of UV light are restricted in an aluminum cavity to avoid the formation opportunity of a noise interference of UV modulation light.

For electric resistance measurement, instead of the conventional pattern for four-point measurement, we designed the ZnO thin film to shape the channel of a thin-film transistor (TFT) [12] shown in Fig. 2. This TFT-type pattern is useful for the measurement of a tiny variation in a large electric resistance, such is the mega-ohm value for the ZnO thin film investigated. To fabricate the ZnO-based TFT, a p-type Si substrate is sputtered with a 150 nm-thick SiO_2 layer as the gate insulator, and a 100 nm-thick ZnO layer was grown on the SiO_2 layer of the TFT to form the channel. Then, Au films are deposited and patterned to mold all electrodes, including source, drain, and gate of the TFT. Finally, post-annealing is performed to reduce the contact resistance of the source and the drain electrodes.

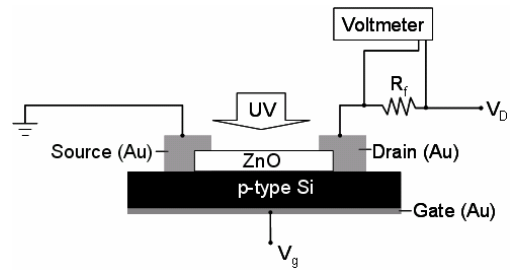


Fig. 2. Scheme of ZnO-based TFT.

The electric resistance of the ZnO thin film is detected by measuring the electric current through the ZnO channel under a given bias voltage. To detect the electric current, a reference resistor with a known resistance R_f is connected in series with the source-ZnO-drain. By measuring the voltage V_R across the reference resistor, the electric current I through the ZnO channel can be obtained via $I = V_R/R_f$. Furthermore, the resistance of the ZnO channel

is found as $(V_D - V_R)/(V_R/R_f)$, where V_D is the voltage across the source-ZnO-drain and the reference resistor in series. As such, for a given V_D , R_f and gate voltage V_g , the V_R 's are measured under UV irradiation to investigate the UV-modulated electric resistance of the ZnO thin film.

3. Results and discussion

The values of the transmission coefficient S_{21} for a green light passing through the ZnO/quartz system under UV irradiation with power densities up to 8.7 W/cm^2 are measured by the heterodyne interferometer and shown in Table 1.

Table 1. Transmission coefficients ($S_{21} = |s_{21}|e^{i(\theta_{21})}$) of ZnO/quartz sample under UV irradiation with various power densities.

UV power density (W/cm^2)	Transmission coefficient $S_{21} = s_{21} e^{i(\theta_{21})}$
0	$0.7196e^{i(52.00^\circ)}$
1.79	$0.7198e^{i(55.84^\circ)}$
3.6	$0.7199e^{i(56.41^\circ)}$
5.28	$0.7201e^{i(60.03^\circ)}$
7.1	$0.7211e^{i(74.65^\circ)}$
8.7	$0.7227e^{i(94.47^\circ)}$

It is found that the amplitude and the phase of the transmission coefficient S_{21} increase with increasing UV power density. The UV-modulated real part ϵ_r and imaginary part ϵ_i of the dielectric constant of the ZnO thin film are obtained using the generalized matrix method and plotted with round symbols in Figs. 3(a) and (b). As can be seen, ϵ_r decreases slightly with increasing UV power density, and an obvious drop in ϵ_r can be observed when the UV power density exceeds 5.28 W/cm^2 , whereas ϵ_i remains almost constant for the UV power density from zero to 8.7 W/cm^2 . Here, although the variation order of ϵ_r in Fig. 3(a) is around 1% in mathematics, it is quite large in physics and has been identified by the application of UV-modulated one-dimensional photonic-crystal resonator for visible lights [14]. In Fig. 3(b), the variation order of ϵ_i is as large as 140 % but viewed as constant without physical meaning, and the reason is that the transparent property of ZnO material in visible range makes ϵ_i small in order of 10^{-6} , which is beyond the accuracy order of 10^{-3} of the adopted common-path heterodyne interferometer. ϵ_r

and ϵ_i , as functions of the UV power density, can be converted to UV-power-density dependent complex refractive index of a ZnO thin film via Eqs. (2) and (3). The real part n_r and the imaginary part n_i of the complex refractive index of a ZnO thin film versus the UV power density are shown with square symbols in Figs. 3(a) and 3(b), respectively. Remarkably, ϵ_i and n_i are much smaller than 1. Since ϵ_i or n_i is related to the dissipation of light energy transmitting through the sample, small ϵ_i and n_i mean that ZnO is almost transparent to the green light. Moreover, ϵ_r and n_r get back to the values without UV irradiation when UV is removed. Hence, the UV-modulated ϵ_r and n_r of ZnO thin films are reversible.

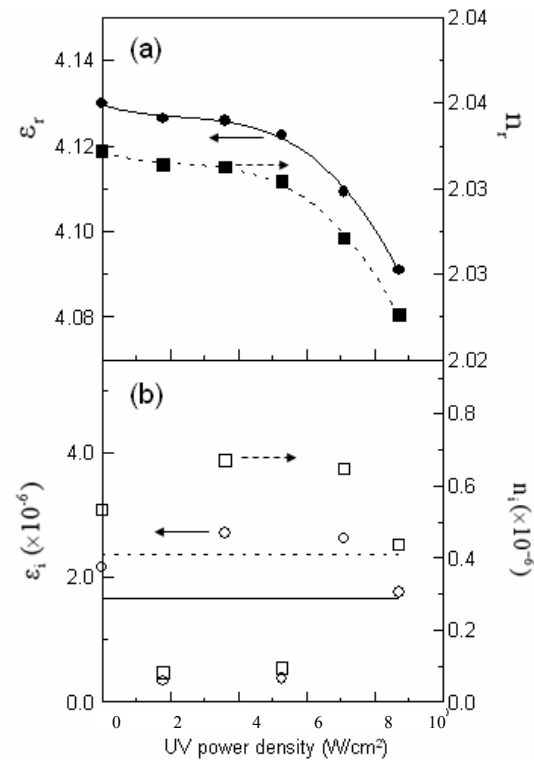


Fig. 3. UV power density-dependences of the real part ϵ_r , n_r (a) and of the imaginary part ϵ_i , n_i (b) of the ZnO thin film.

Since the real part ϵ_r of the dielectric constant is associated with the charge density of bounded electrons, or the so-called valence electrons, the reduction in ϵ_r of a ZnO thin film under UV irradiation implies that the charge density of valence electrons is reduced. It is well-known that electric band gap of ZnO corresponds to UV light. As such, it is suggested that the valence electrons absorb the irradiated UV light to become conduction electrons. In this case, the electric resistance of ZnO thin films should be decreased under UV irradiation. To prove the deduction, the ZnO thin film is designed as a channel of the TFT shown in Fig. 2, and the electric resistances of the ZnO

channel under UV irradiation are measured.

Fig. 4 displays the electric resistance of ZnO thin film as a function of the UV power density for various gate voltages of 0 and 5 V. In general, the gate voltage induces some electrons in the channel and then results in the decrease of electric resistance of the channel to turn on TFT transistor. However, in Fig. 4, for a given gate voltage, the electric resistance of ZnO decreases with increasing UV power density. In other words, the intensity of UV light acts likewise the gate voltage to induce electrons in the channel. This result coincides with the deduction described above. Therefore, the up-conversion of electrons of ZnO thin films from valence bands to conduction bands activated by absorbing UV light contributes to the reduction in the ϵ_r and n_r of ZnO thin film. This mechanism explains also the ZnO photoconductivity when illuminating with UV light [10].

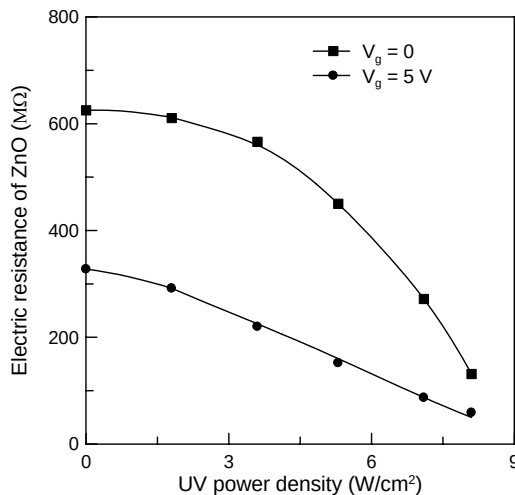


Fig. 4. Electric resistance of ZnO thin film versus the UV power density at various gate voltages (V_g).

4. Conclusions

The dielectric constant or the refractive index of ZnO thin film is reduced under UV irradiation. This reduction is temporary, which means that the modulated dielectric constant or the refractive index of ZnO thin films recovers when the UV light is removed. It is further clarified that the physical origin of the modulated dielectric constant or the refractive index is the up-conversion of electrons of ZnO thin films from valence bands to conduction bands activated by absorbing UV light. Such a property as UV-modulated refractive index of ZnO thin film is promising for developing tunable photonic devices and UV detector.

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