Critical point analysis of dielectric constant in ZnO thin films on different electronic environments

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Abstract. We study the effects of different electronic environments on excitonic properties of ZnO thin films. The thin films were deposited on Si and SiO₂ substrates using DC-unbalanced magnetron sputtering at room temperature. Optical properties of ZnO were measured by spectroscopic ellipsometry with the energy range from 1.2 to 6.5 eV. Spectroscopic ellipsometry data were modelled by Tauc-Lorentz and Gaussian oscillators to obtain the complex dielectric function. To extract the excitonic properties, the dielectric function was analysed by critical point line shapes. The results show that the excitonic states of ZnO/SiO₂ are stronger and shifted to the lower energy, as compared to ZnO/Si. We find that electron transfer occurs from Si substrate to the ZnO films. The electron transfer then reduces the binding energy of exciton in ZnO/Si system owing to electronic blocking effect. Our results reveal that the different electronic environments affect the excitonic properties of ZnO, which is important for optoelectronic applications.

1. Introduction
Zinc Oxide (ZnO) is a group II-IV semiconductor material that gains great interest in various application such as optoelectronic devices [1], sensors [2-3], spintronics [4], and photovoltaics [5] owing to its promising properties such as wide direct band gap (3.37 eV) at room temperature, generally n-type semiconductor material [6-7], a good transparency at visible spectrum and near UV [8], and large excitonic binding energy (60 meV) that allows excitonic emission can occur at room temperature or even higher [9-10]. One of the interesting applications is in the optoelectronic devices and focused on the excitonic emission [11]. The previous research reported that the excitonic states of ZnO can be modified by using the different substrates such as metal (platinum) and insulator (quartz) due to electronic blocking effect [12-13]. The electronic blocking effect in the metal substrate is stronger than that of insulator caused by the number of the transferred free electron from the metal substrate more than the insulator substrate. [14]. It shows that the substrate has an important role in controlling the excitonic states of ZnO-based thin films. However, the effect of insulator and semiconductor substrates on the excitonic states of ZnO thin film has not been reported.

In this study, we investigate the excitonic states and optical constants of ZnO thin films on insulator (SiO₂) and semiconductor (Si) using spectroscopic ellipsometry. The optical constant such as the complex dielectric function is analysed using Tauc-Lorentz and Gaussian oscillators. The critical point (CP) is used to study the electron transfer phenomena and the excitonic transitions of ZnO.
2. Experimental Methods

ZnO powder with high purity (99.9%) was ground and pressed to form a pellet. Afterwards, the pellet was sintered in the furnace at 1000 °C for 10 hours in order to get the sputtering target with high quality. Silicon p-type with (100) orientation was used for the substrates and was cleaned by RCA procedure. SiO$_2$ substrate was obtained via dry oxidation process of silicon substrate at 1000 °C for 5 minutes. ZnO thin films were deposited on the Si and SiO$_2$ using DC-Unbalanced Magnetron Sputtering (DC-UBMS) method. The deposition process was performed for 4 hours at room temperature. During the growth process, the Ar flow rate of 100 sccm, the chamber pressure of 3×10$^{-2}$ mbar, the applied voltage of 480 V, and the current of 25 mA were kept constant.

The crystal structure of ZnO thin films was analysed using X-ray Diffraction (XRD). The morphological features of ZnO thin films were studied using scanning electron microscopy (SEM), and spectroscopic ellipsometry (SE) with the energy range from 1.2-6.5 eV was used for the optical characterization of films. Three incident angles have been used to perform the SE measurement i.e 50°, 60°, and 70° to get the raw measurement SE output ψ and Δ. The optical model of ZnO/Si and ZnO/SiO$_2$ are constructed by taking into account the surface roughness as shown in Figure 1. The optical properties of the material are obtained by fitting the experimental data with Tauc-Lorentz and Gaussian oscillators. The imaginary part of dielectric function for Tauc-Lorentz oscillator is formulated in equation 1 [15].

$$
\varepsilon_{2_{\text{T}}} (E) = \begin{cases} 
\frac{A_{\text{T}} E_{\varepsilon_{\text{T}}} B_{\text{T}} (E - E_g)^2}{E \left( (E^2 - E_{\varepsilon_{\text{T}}}^2)^2 + B_{\text{T}}^2 E^2 \right)} & E > E_g \\
0 & E \leq E_g 
\end{cases},
$$

where $A_{\text{T}}$, $E_{\varepsilon_{\text{T}}}$, $E_g$, and $B_{\text{T}}$ represent the amplitude, position, band gap, and broadening parameters, respectively. Furthermore, For the Gaussian oscillator, the imaginary part of dielectric function is shown in equation 2 [15].

$$
\varepsilon_{2_{\text{G}}} (E) = A_G e^{-\left(\frac{E - E_{\varepsilon_{\text{G}}}}{\sigma}\right)^2} - A_G e^{-\left(\frac{E + E_{\varepsilon_{\text{G}}}}{\sigma}\right)^2}, \sigma = \frac{B_G}{2\sqrt{\ln 2}},
$$

where $A_G$ is the amplitude, $E_{\varepsilon_{\text{G}}}$ is the position, and $B_G$ is the broadening parameter.

![Figure 1](image-url) Scheme of the optical model used for the fitting process in SE analysis.
3. Results and Discussions

The crystallinity of ZnO thin films grown on Si and SiO$_2$ substrates are analysed by XRD pattern as shown in Figure 2. Three peaks of (100), (002), and (101) are observed for ZnO/Si and ZnO/SiO$_2$, which exhibit hexagonal wurtzite structure [16]. The highest intensity of ZnO/Si XRD pattern is (100) plane. However, the ZnO/SiO$_2$ film shows the highest intensity in (101) plane.

![Figure 2. XRD patterns of ZnO thin films grown on Si and SiO$_2$ substrates.](image)

The surface morphology of ZnO thin films was analysed by SEM image operated at 5.0 kV voltage. Figure 3 shows the SEM images of ZnO thin films on Si and SiO$_2$ substrates. The microstructures of the films consist of non-homogenous grains distributed along the surface. It shows that the grain size and the non-uniformity of the structure are independent of the substrate used [17].

![Figure 3. SEM images of the ZnO thin films (a) on SiO$_2$ and (b) Si substrates.](image)

The optical properties of ZnO thin films were analysed by spectroscopic ellipsometry (SE). Since the SE measurement is an indirect technique, fitting the SE data of $\psi$ and $\Delta$ with the proper optical model is needed to obtain the optical constant of ZnO thin films. Tauc-Lorentz and Gaussian models were used to perform the fitting process and to obtain the information related to the surface roughness...
and film thickness. Figure 4 shows the fitting results of $\psi$ and $\Delta$ for ZnO/Si and ZnO/SiO$_2$ respectively with the energy range of 1.2-6.5 eV.

![Figure 4](image)

**Figure 4.** Fitting result of (a,b) ZnO/Si and (c,d) ZnO/SiO$_2$ with multiple incident angles ($50^\circ$, $60^\circ$, and $70^\circ$).

![Figure 5](image)

**Figure 5.** Second derivative spectra of (a) the real and (b) imaginary parts of the dielectric function for ZnO/Si and ZnO/SiO$_2$ systems. Inset of (b) shows the imaginary part of the dielectric function for ZnO/Si and ZnO/SiO$_2$ systems.
To study the optical transitions that occur on ZnO films, the critical point (CP) analysis of dielectric function was used with the energy range from 2.5 to 4.0 eV as shown in Figure 5. The CP parameters were extracted by fitting the second derivative spectra with the standard analytic least square scheme. The formulation is shown in equation 3, where $A$ is the amplitude, $\Gamma$ is the broadening parameter, $E$ is the energy, and $\phi$ represents the excitonic phase angle [18]. The $n$ values of $-1$, $-\frac{1}{2}, 0, \frac{1}{2}$ represent 1D, 2D, 3D critical points, and discrete exciton, respectively. The best fit is obtained with $n=1$ that represents excitonic transition occurs in ZnO films. The CP parameters are summarized in Table 1. In ZnO/SiO$_2$, the excitonic peak significantly increased and shifted to lower energy. The broadening parameter becomes narrower, indicating the lifetime of exciton in ZnO/SiO$_2$ system is longer than that of ZnO/Si [19].

$$\frac{d^2\varepsilon}{dE^2} = \begin{cases} n(n-1)Ae^{i\phi}(E - E_g + i\Gamma)^{n-2} & n \neq 0 \\ A e^{i\phi}(E - E_g + i\Gamma)^{-2} & n = 0 \end{cases}$$  \hspace{1cm} (3)

**Table 1.** The fitting parameters of CP analysis from 2.5 eV to 4.0 eV.

| Parameters | ZnO/Si | ZnO/SiO$_2$ |
|------------|--------|-------------|
| $A$        | 0.13   | 0.24        |
| $E$ (eV)   | 3.35   | 3.28        |
| $\Gamma$ (eV) | 0.23  | 0.15        |
| $\phi$     | 7.88   | 4.34        |

*Figure 6. Schematic model of electron transfers for ZnO films grown on (left) Si and (right) SiO$_2$ substrates.*
Figure 6 shows the schematic model of electron transfer on ZnO/Si and ZnO/SiO$_2$ system. The photon energy range which is used in this experiment is ranging from 1.2 eV to 6.5 eV. This energy range is enough to excite the electron from the valence band to the conduction band of silicon (band gap = 1.1 eV). The free electron from Si substrate is easily transferred to the ZnO film and makes the film become more conductive. This free electron also may block the electron-hole pairs in ZnO films, which is called electronic blocking effect. However, these phenomena do not occur in ZnO/SiO$_2$ system, because of the high potential barrier from SiO$_2$ (band gap = 8.9 eV). The potential barrier will block the free electron from silicon. Table 2 shows the comparison of the excitonic peak of ZnO on various substrates obtained from $\varepsilon_2$ spectra, as compared to the previous study. It is clearly observed that the excitonic transitions of ZnO on metal substrate is strongly suppressed than the others substrate due to the huge amount of free electron of metal compare than others.

| Table 2. The excitonic transitions of ZnO in various substrates. |
|---------------------------------|------------|---------------|
| Deposition Methods             | Substrates                  | The peak of $\varepsilon_2$ in the ZnO band gap region |
| Sputtering                      | SiO$_2$ (Insulator)            | 1.9            |
| Sputtering                      | Si (Semiconductor)           | 1.7            |
| Pulsed Laser Deposition [14]    | Platinum bulk (Metal)        | 2              |
| Pulsed Laser Deposition [14]    | Quartz (Insulator)            | 3.5            |

4. Conclusions
The electronic blocking effect on the excitonic states of ZnO/Si and ZnO/SiO$_2$ have been studied using critical point (CP) analysis. The crystallinity of ZnO films is analysed by XRD and shows that the ZnO films have hexagonal wurtzite structure. SEM measurement shows that the ZnO films are grown non-uniformly on Si and SiO$_2$ substrates. The optical properties of ZnO thin films are investigated by spectroscopic ellipsometry. CP analysis is used to study the excitonic properties. From the fitting results of CP analysis, the amplitude of ZnO/SiO$_2$ is higher than that of ZnO/Si, and the broadening parameter of ZnO/SiO$_2$ is narrower than that of ZnO/Si, indicating the increase of the excitonic transition and exciton lifetime in ZnO/SiO$_2$ system. This behaviour is due to the high potential barrier from SiO$_2$, making the electronic blocking effect is not observed in this system.

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