

Slow oscillations in the low-temperature optical reflectance spectra of ZnO: Surface space-charge effect

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Low-temperature optical reflectance spectra from (10 $\bar{1}0$) surface of a ZnO crystalline rod were measured at near normal incidence. These spectra show slow oscillations which originate from the interference between lights reflected from the front surface and the second surface of a space-charge double layer formed on ZnO (10 $\bar{1}0$). It is found that the oscillation period is linearly dependent on the wavelength of light. The expanding rate of the space-charge double layer is estimated to be 1.3 nm/min. © 2007 American Institute of Physics. [DOI: 10.1063/1.2472523]

ZnO is a direct wide band gap semiconductor with wurtzite (hexagonal) crystalline structure. Compared with other semiconductor materials, ZnO possesses several unique properties such as an extremely large exciton binding energy of 60 meV. This leads to highly efficient light emission at room temperature or above. In addition, its electron drift mobility saturates at a higher electric field and at a higher value, which makes it attractive for high frequency electronic devices. Currently, ZnO is attracting considerable research interests due to these superior properties.

The surfaces of a semiconductor can be important for device operations as most, if not all, semiconductor devices operate by invoking some kind of nonequilibrium process that occurs at the surface.¹ It has been long known that a space-charge double layer can be formed on the surface of a semiconductor via, e.g., preferential adsorption of foreign ions or adequate light illumination. The presence of a space-charge double layer can strongly affect the optical and electrical properties of the semiconductor. It is a subject of considerable attention from both fundamental science and application points of view. For ZnO, however, studies on the surface space-charge effect remain limited. In this letter, we present such a study by using the low-temperature optical reflectance spectroscopy. The reflectance spectra exhibit a wavelength dependent slow oscillation, indicating the presence of a time-varying space-charge double layer on the illuminated surface of ZnO. Some important information such as the thickness variation rate of the space-charge double layer can be extracted from the oscillation structure.

The sample studied in the present work was a single-crystal hexagonal rod grown along the *c* axis with a diameter of about 3 mm. For low-temperature optical reflectance measurements, the sample was mounted on the cold finger of a Janis closed circle cryostat with a varying temperature in the range of 8–330 K. The monochromatic light dispersed from a xenon lamp with an Acton SP300 monochromator was guided almost normally (incident angle of $\sim 10^\circ$) onto the (10 $\bar{1}0$) surface of the sample. The reflected light from the sample surface was detected by a Hamamatsu Si *p-i-n* diode. The reflectance spectra in the spectral range from

350 to 700 nm were measured. Within this wavelength range, a fraction of the incident light is reflected from the front surface of the sample, while another fraction penetrates through the sample and is then reflected by the rear surface of the sample. These reflected lights from the two parallel surfaces are spatially well separated and distinguishable.

Figure 1 shows several reflectance spectra from the front surface of the sample at different temperatures. The spectra were shifted along the vertical direction for clarity. In addition to the double structure at ~ 361 and 366 nm, which are, respectively, the *A* and *B* exciton resonances, the spectrum measured at 8 K exhibits a clear oscillation structure. When the temperature is increased up to 40 K and above, however, the oscillation structure disappears. The oscillation structure seen at low temperatures suggests an interference effect. Since the reflected light beams from the front and rear surfaces of the sample are well separated spatially due to the large sample thickness (~ 3 mm) of the rod, the interference effect cannot be due to lights reflected from such surfaces. Instead, we suggest that a space-charge double layer structure is formed at the illuminated front surface of the sample, which is responsible for the observed oscillatory behavior in reflectance spectra. It is further noted that the low-temperature oscillatory reflectance show a clear time variation as depicted in Fig. 2, which presents a series of spectra taken at a time interval of 10 min consequentially from the top spectrum to the bottom one. In Fig. 3, we plot the reflectance

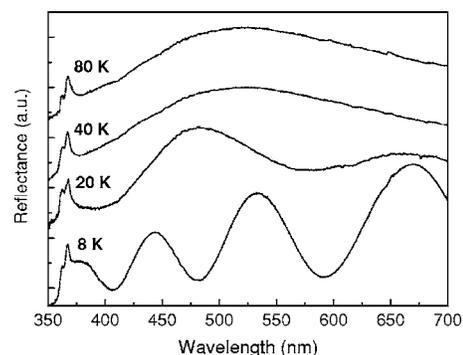


FIG. 1. Measured reflectance spectra from ZnO (10 $\bar{1}0$) surface at different temperatures. At temperatures below 40 K, the spectra show an oscillatory behavior.

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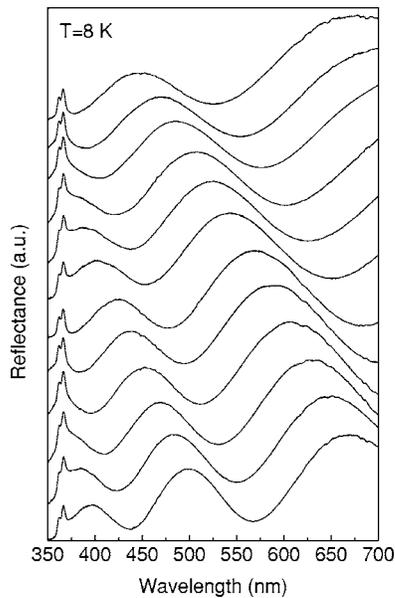


FIG. 2. Series of reflectance spectra measured at a time interval of 10 min consecutively from the top to bottom.

tion intensity as a function of time for a few selected incident light wavelengths, which exhibits a well-defined oscillatory behavior. In the figure, the open circles represent the experimental data while the solid lines are the fitting curves using the cosine function. The oscillation period is seen to depend strongly on the wavelength of the incident light. For example, it is about 96 min for the light of 500 nm in wavelength while it is 136 min for the 700 nm one.

It is known that crystalline ZnO surface can support extremely strong electron accumulation layers. For example, surface electron densities up to $2 \times 10^{14} \text{ cm}^{-2}$ have been achieved,²⁻⁵ which are an order of magnitude higher than that attained in other systems such as GaAs/Al_xGa_{1-x}As interface, InAs(110) surface,⁶ and InAs oxide interface.⁷ Space-charge double layer at ZnO surface can be easily produced by irradiation with electrons or light^{8,9} as well as by exposure to atomic hydrogen or He ions. In the present ex-

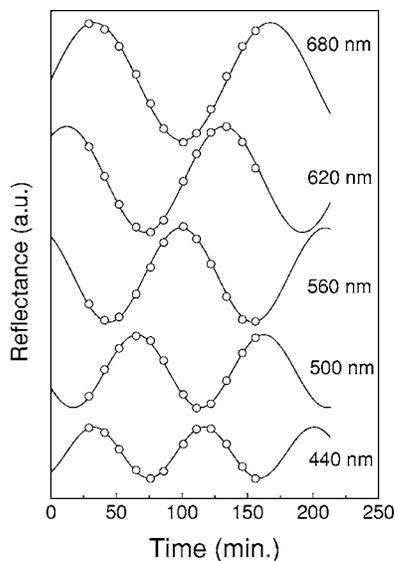


FIG. 3. Reflectance intensity for different wavelengths of the incident light measured at different times. The open dots represent the experimental data while the solid lines are the fitting curves using a cosine function.

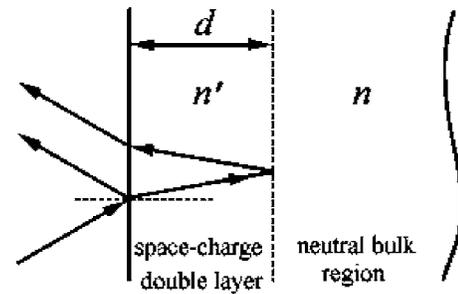


FIG. 4. Schematic diagram showing the space-charge double layer formed on ZnO surface and the interference effect.

periment, the space-charge double layer on ZnO surface is believed to be created by light illumination at low temperature and in vacuum.

According to Garrett and Brattain,¹⁰ a space-charge double layer can arise due to the so-called surface photoeffect on the surface of a semiconductor under the illumination of light. As a result of the surface charge layer formation, the dielectric properties such as the refractive index in this region will be different from that in the interior of the semiconductor. Figure 4 schematically sketches such a space-charge double layer with width d , whose average refractive index is denoted by n' . Under normal incidence of light, the reflectance intensity can be written as¹¹

$$R = \bar{R}[1 + 2C \operatorname{Re}\{re^{2i\phi}\}], \quad (1)$$

where $\bar{R} = [(n' - 1)/(n' + 1)]^2$, $C = -4n'/(n'^2 - 1)$, Re represents the real part, r is a complex quantity denoting the coefficient of reflection from the neutral bulk region with refractive index n , while ϕ is the phase shift of the light wave after its passage through the space-charge double layer, which can be expressed as

$$\phi = \frac{2\pi n' d}{\lambda}. \quad (2)$$

Equation (1) can be rewritten as

$$R = \bar{R} + \Delta R \cos\left(\frac{4\pi n' d}{\lambda}\right), \quad (3)$$

where $\Delta R = 2C|r|$. Equation (3) can describe the observed oscillation behavior of the low-temperature reflectance spectra quite well. It suggests that for a fixed thickness of the space-charge double layer d , the reflectance oscillates with wavelength of λ . For a given wavelength, on the other hand, if the thickness of the space-charge double layer happens to vary with time, the reflectance will also oscillate with time.

According to Eq. (3), the overall reflectance is the sum of the background reflectance \bar{R} and an oscillatory term. The latter originates from the Fabry-Pérot-type interference due to the presence of the space-charge double layer, resulting in an overall reflectance that is modulated in the form of a cosine function with amplitude ΔR . From Fig. 3, it is reasonable to assume that both \bar{R} and ΔR are unchanged for a given wavelength during the time interval of measurements. So the reflectance oscillation with time is mainly due to the variation of the space-charge layer thickness d . The nice fitting of the oscillation traces by the cosine function suggests a con-

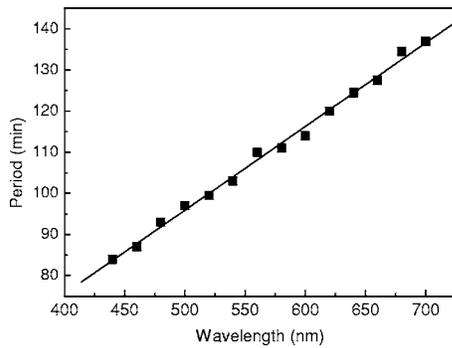


FIG. 5. Time periods of the oscillations plotted against the incident light wavelength. The solid squares represent the experimental data while the solid line is a linear fitting to the data.

stant increasing rate of the double layer thickness. Assuming that the growth rate of the space-charge layer is g , Eq. (3) can then be expressed as

$$R = \bar{R} + \Delta R \cos\left(\frac{4\pi n' g t}{\lambda}\right), \quad (4)$$

from which, one may deduce the oscillation period as being

$$T = \frac{\lambda}{2n'g}. \quad (5)$$

If the dispersion of n' is negligible and the expanding rate g of the space-charge layer is constant, then the oscillation period T will become linearly proportional to wavelength λ . This explains why the oscillations at longer wavelength exhibit larger period, as shown in Fig. 3. It also accounts for the evolution of the oscillation traces with time shown in Fig. 2.

Figure 5 shows the time periods of the oscillations determined by curve fitting versus the wavelength of the incident light. The solid squares represent the experimental data and the solid line is a linear fitting. From the figure, the linear dependence of the oscillation periods on wavelength is

confirmed. Assuming that n' does not change appreciably over the wavelength range, such a linear relation between T and λ will suggest a constant rate of expansion of the space-charge double layer with time.

To estimate the expanding or growth rate g , we note that the slope of the line in Fig. 5 should be $1/2n'g$ according to Eq. (5). Taking $n'=2$, a reported value of refractive index of ZnO at the 600 nm wavelength of light,¹²⁻¹⁴ we derive that $g=1.3$ nm/min. In other words, the thickness of the space-charge double layer expands by 156 nm during the 2 h long measurements. It can be expected that this time-varying space-charge double layer will have strong influence on the electrical and optical properties of ZnO.

In conclusion, we have observed a slow oscillation behavior of the reflectance spectra of ZnO at low temperatures. The time periods of oscillations are found to be wavelength dependent. This oscillatory reflectance is attributed to the Fabry-Pérot interference due to the existence of a space-charge double layer on the illuminated surface of ZnO. The thickness of the space-charge double layer grows at about 1.3 nm/min.

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