Dielectric spectroscopy studies of ZnO single crystal*

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Dielectric relaxation and charge transport induced by electron hopping in ZnO single crystal are measured by using a novocontrol broadband dielectric spectrometer. Typical Debye-like dielectric relaxation originating from electronic hopping between electronic traps and conductive band in surface Schottky barrier region is observed for ZnO single crystal-Au electrode system. However, after insulation of ZnO single crystal by heat treatment in rich oxygen atmosphere, dielectric relaxation and alternating current conductance are observed simultaneously in the dielectric spectra, implying that dielectric relaxation and charge transport can be induced simultaneously by electronic hopping at high temperature in an ordered system. The intrinsic correlation between local dielectric relaxation and long range charge transport offers us a new method to explore complicated dielectrics.

Keywords: ZnO single crystal, electronic hopping, conductance, dielectric relaxation

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1. Introduction

A dielectric spectrometer is a convenient and effective tool to measure macroscopic dielectric properties without any damage to the sample. From dielectric spectra, some important microscopic information about electric polarization originating from local reciprocating motion of bound charge and electric transport originating from the long range drift motion of free charge can be obtained.[1–3] It seems that there is no relation between electric polarization and electric transport. However, the coexistence of electric polarization and electric transport originating from the hopping of weakly bound charge at low temperature in an unordered system is found, which implies the coupling of local dielectric relaxation and nonlocal charge transport. However, whether there still exists the coupling effect of dielectric relaxation and charge transport at high temperature, for example at room temperature, is not clear at present. Especially, the case of an ordered system is not investigated at all.

Electronic relaxation, originating from electronic hopping between the point defect energy level and the conductive band at the depleted layer, is a very common phenomenon in electronic ceramics,[1] which in fact is a kind of hopping process of weakly bound electrons at high temperature in an ordered system. However, the effect of electronic relaxation is regarded as a pure electric polarization process[1] and charge transport characteristics have not been investigated at all.

In this paper, dielectric relaxation characteristics and charge transport characteristics are observed at the same time in ZnO single crystal after heat treatment in an oxygen-rich atmosphere, implying that dielectric relaxation and charge transport in ZnO have the same origin from electronic hopping between the intrinsic point defect energy level and the conductive band. The results in this paper help to improve the study of the coupling of dielectric relaxation and charge transport.

2. Experiment

N-type ZnO single crystals were provided by Hefei Kejing Ltd. Co. Its size is 10 mm × 10 mm × 0.8 mm and its crystal orientation is along (1111). Au electrodes were prepared by sputtering and a Schottky barrier may build between ZnO and Au electrodes. In order to eliminate the interfacial effect, some ZnO single crystals were insulated by heat treatment in an oxygen-rich atmosphere. Dielectric frequency spectra were measured using a novocontrol broadband dielectric spectrometer from 0.1 Hz to 10^7 Hz in the temperature range from –140 °C to 30 °C.

3. Results and discussion

3.1. Dielectric properties of ZnO single crystal

Dielectric spectra of ZnO single crystal are shown in Figs. 1(a) and 1(b). A step-like decrease in the ε'–f curve indicates a dielectric relaxation process. The dielectric constant of ZnO single crystal is about 1000, which is much higher than the intrinsic value of about 10. This implies that a Schottky barrier exists in the surface of a ZnO grain due to the difference in work function between ZnO and Au or the existence of surface states. Obviously, the large dielectric constant of about 1000 originates from the boundary layer capacitor (BLC) effect. However,

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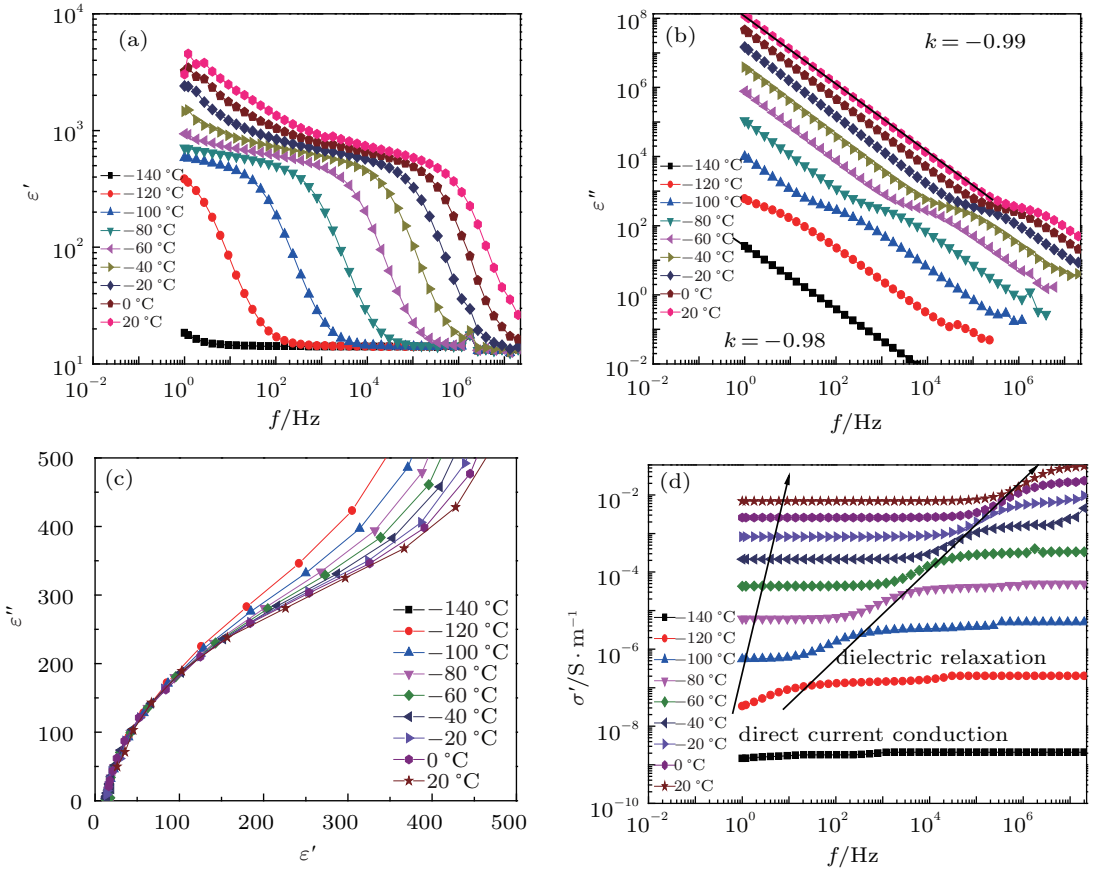


Fig. 1. (color online) Dielectric properties of ZnO single crystal: (a) dielectric constant, (b) dielectric loss, (c) Cole–Cole pictures, (d) conductivity.

the corresponding relaxation peak in the ε''–f curve is not clear, which implies that the influence of direct current conduction cannot be omitted. According to Debye theory, dielectric loss can be expressed as follows:

$$\varepsilon'' = \frac{\gamma + g}{\omega\varepsilon_0} = \frac{\gamma}{\omega\varepsilon_0} + \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2}, \tag{1}$$

where γ and g are the direct current conductivity and the relaxation conductivity respectively, ω is the angular frequency, ε_0 is the vacuum dielectric constant, ε_s and ε_∞ are the static dielectric constant and the light frequency dielectric constant respectively. The first item on the right-hand side of the above equation corresponds to the contribution of direct current conductivity, which inversely decreases with frequency. The second item is the contribution of dielectric relaxation, which is proportional to frequency at low frequency. Therefore, the total dielectric loss follows the law of $\varepsilon'' \propto \omega^{-1}$ at low frequency. The slopes in low frequency and high frequency regions of ε''–f curve are almost the same, i.e., –1 and do not change at all with temperature. Cole–Cole arcs at different temperatures are shown in Fig. 1(c). The coincidence of the arcs with each other indicates that the relaxation is of Debye type and ε_s and ε_∞ do not change with temperature. However, the Cole–Cole curve increases rapidly and changes from a convex shape into a concave shape in the low frequency region. If there is another Cole–Cole arc in the lower frequency region, the curve should be convex, which is contrast to the experimental results. In fact, it can be confirmed theoretically that for a Debye type dielectric relaxation process, $d\varepsilon''/d\varepsilon' < 0$ when $\omega\tau \ll 1$. So it can be concluded that the rapid increase in the low frequency region of Cole–Cole curve comes from direct current conduction.

Conductivity σ' can be obtained by multiplying both sides of Eq. (1) with $\omega\varepsilon_0$ and given as

$$\sigma' = \omega\varepsilon_0\varepsilon'' = \gamma + g = \gamma + \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{\tau}\frac{(\omega\tau)^2}{1 + (\omega\tau)^2}. \tag{2}$$

It is clear from the above equation that the direct current conductivity does not vary with frequency, while relaxation conductivity increases with frequency increasing and tends to be saturated in the end. A step-like curve of $\ln\sigma'$–$\ln f$ is expected and shown in Fig. 1(d). The flat region at low frequency, which is invariable with frequency, corresponds to direct current conductivity. The height of the step represents the saturated relaxation conductivity. According to Eq. (2), the saturated relaxation conductivity can be expressed as follows:

$$g_{\max} = \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{\tau} = \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{\tau_0}\exp\left(-\frac{u}{kT}\right), \tag{3}$$

where u is the relaxation activation energy, k is the Boltzmann constant, T is the absolute temperature. From the

slope the $\ln(g_{max})$–$1/T$ relaxation activation energy is obtained to be 0.34 eV. According to the trapped electron relaxation mechanism in the Schottky barrier region, it is found by dielectric spectroscopy that the characteristic loss peak of ZnO originates from native defects of interstitial Zn and vacancy oxygen with activation energies of 0.26 eV and 0.36 eV respectively.[1] The existence of vacancy oxygen has been revealed by photoluminescence (PL) spectroscopy and other experiments.[1,4–9] Since the trap energy level E_T in the forbidden band is almost fixed for a certain material, the activation energy $(E_C–E_T)$ for trapped electron relaxation is almost invariant.[1,10] Therefore, it can be deduced reasonably that the loss peak in ZnO single crystal originates from oxygen vacancies.

Electronic hopping in the Schottky barrier region occurs at the point of intersection of Femi energy level and point defect energy level when an alternating current electric field is applied. Since the hopping direction of an electron weakly bound by an intrinsic point defect is perpendicular to the applied electric field, charge transport cannot be induced at all. However, the electronic relaxation phenomenon is induced, which is equivalent to the Debye-type dielectric relaxation process.[1]

3.2. Dielectric properties of ZnO single crystal after heat-treatment in oxidizing atmosphere

After heat treatment in rich oxygen atmosphere, dielectric properties of ZnO single crystal are shown in Fig. 2. Dielectric

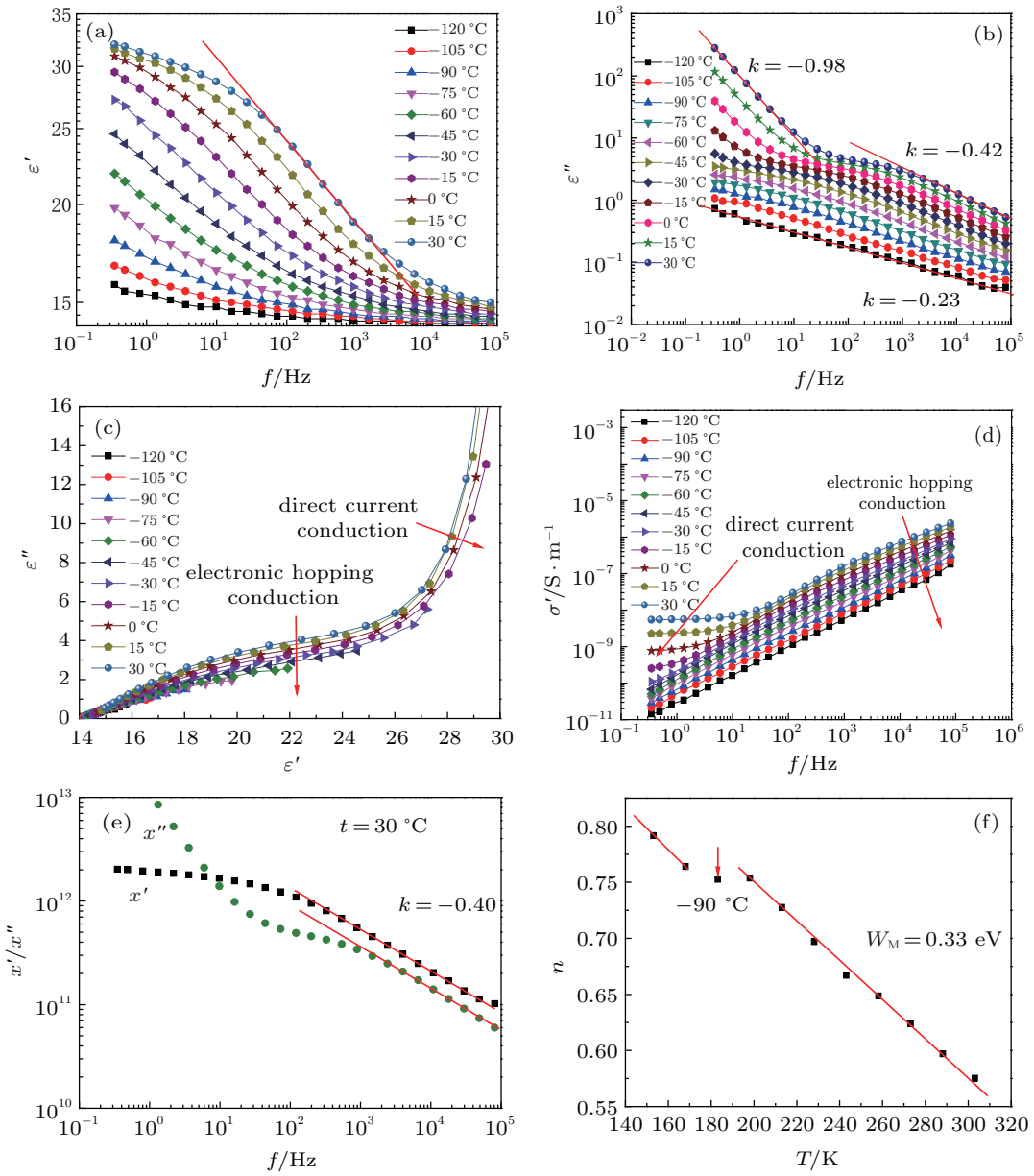


Fig. 2. (color online) Dielectric properties of ZnO single crystal after heat treatment in oxygen atmosphere: (a) dielectric constant ε', (b) dielectric loss ε'', (c) Cole–Cole pictures, (d) conductivity σ', (e) permittivity, and (f) activation energy of electronic hopping.

relaxation occurs at lower frequency, and dielectric constant is only about 30, which is similar to the bulk dielectric constant of ZnO. This implies that ZnO single crystal becomes an insulator and the Schottky barrier disappears after heat treatment.

The dielectric constant decreases linearly with frequency increasing in double logarithmic coordinates as shown in Fig. 2(a), which fits the universal equation of alternating current conductivity $\sigma = A\omega^n$ very well.[11–14] Especially, dielectric loss decreases linearly with frequency increasing in double logarithmic coordinates and the corresponding slope drops off also with the increase of temperature as shown in Fig. 2(b). Compared with Fig. 1(c), Cole–Cole picture of ZnO single crystal after heat treatment is a little diverged and the dielectric loss increases obviously with temperature increasing as shown in Figs. 2(c) and 2(d). This implies that the dielectric relaxation process is accompanied with charge transport process. Another evidence of alternating current conductivity is that the real and imaginary components of permittivity decrease linearly with frequency increasing and the corresponding slopes are the same as shown in Fig. 2(e). As is well known, that the weakly bound charge in ZnO single crystal is electron bound by intrinsic point defects, such as oxygen vacancy as discussed above. Therefore, alternating current conductivity in ZnO single crystal is induced by electronic hopping.

After heat treatment, ZnO becomes an insulator and no Schottky barrier exists in its surface. With an applied electric field, the energy band of ZnO is inclined. Under the incentive of temperature, some weakly bound electrons get rid of the constraint of intrinsic point defect and enter into the conductive band. The electrons in the conductive band drift along the reverse direction of the applied electric field and are trapped by point defects again. In these processes, dielectric relaxation and charge transport are formed at the same time and both of them have the same activation energy. With the increase of temperature, more electrons enter into conductive band and electronic hopping is more apparent, as shown in Fig. 2.

The slope is obviously higher than –1 in the high frequency region of the ε''–f curve and the slope decreases with temperature increasing, which fits the characteristics of hopping conductivity with respect to frequency and temperature very well. Another proof is that the conductivity is not saturated in the high frequency region but increases rapidly with frequency increasing. The corresponding exponent index decreases from 0.79 at –120 °C to 0.57 at 30 °C as shown in Figs. 2(b) and 2(d).

Pike[15] proposed that the mechanism of electronic hopping is near-neighbor hopping if the temperature is not low enough. In this model, the electrostatic potential of an electron bounded by a point defect can be expressed as

$$W = W_{\mathrm{M}} - \frac{4e^2}{\varepsilon R}, \tag{4}$$

where W_{M} is the ionization energy, W the barrier height for electronic hopping, ε the dielectric constant, and R the distance between neighboring equilibrium positions. According to Pike's model, the index n in the hopping conduction mechanism is[15]

$$n = 1 - \frac{6kT}{W_{\mathrm{M}}}. \tag{5}$$

Therefore, n can be obtained by the slope of $\ln\sigma$–f curve. Furthermore, ionization energy W_{M} can be calculated from n–T curve. As shown in Fig. 2(e), W_{M} is 0.33 eV, which is close to the first ionization energy of the oxygen vacancy. This implies that electronic hopping occurs between the oxygen vacancy and the conductive band. In the curve of n–f, there is an inflection point at –90 °C. This demonstrates the difference in the mechanism of electronic hopping between in the high temperature region and in the low temperature region.

4. Conclusion

Dielectric relaxation characteristics and charge transport characteristics of the electronic hopping process are investigated in ZnO single crystal. It is found that the electronic hopping between the intrinsic point defect energy level and the conductive band in the Schottky barrier region gives rise to dielectric relaxation only, while the in-grain electronic hopping will induce dielectric relaxation and charge transport simultaneously. The results in this paper help to improve the study of coupling of dielectric relaxation and charge transport.

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