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Dielectric studies of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ epilayers

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Abstract

We report on the dielectric properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ ($0.015 < X < 0.048$, $0.003 < Y < 0.103$) epilayers, investigated by capacitance (C) and dissipation factor (D) measurements in the temperature range 180–460 K and in the frequency range 20 Hz–100 kHz. A Debye relaxation behavior of the polarization has been observed, with the relaxation time decreasing very quickly with increasing temperature. We found that the activation energy decreases with increasing Mn concentration and Te concentration. In the capacitance measurements, this energy increases with decreasing test frequency. The deduced activation energy from capacitance is consistent with that of the dissipation factor. We suggest that carrier hopping among structural defects can be used to interpret our results. The change of the activation energy with Mn and Te concentration is explained in terms of the four-center model, in which if the number of Mn or Te atoms increases in the nearest-neighbor sites of the defect, it can have four possible configurations. The measured defect behavior reflects the overall average of all energy levels involved in the center, and the result is weighted by the relative concentrations. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Diluted magnetic semiconductors (DMS) are compound semiconductor alloys with a fraction of ions replaced by the magnetic transition-metal ions [1–4]. DMS have attracted a great deal of attention due to their unique magnetic properties as well as potential application [2–4]. Many different techniques have been used to probe the properties of DMS. However, the study of the dielectric properties are rather limited [1]. It is known that dielectric study can reveal many information of a solid, such as phase transition, defect, and transport properties. In this paper, we report the dielectric properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ ($0.015 < X < 0.048$, $0.003 < Y < 0.166$) epilayers through the measurements of capacitance and dissipation factor at different temperatures and frequencies. A Debye-like relaxation in the dielectric response has been observed, and the relaxation rate is thermally activated. It is found that the obtained activation energy decreases with increasing Mn and Te concentrations.

A microscopic structure of the defects based on the four-center model is proposed to explain our observation [1].

To illustrate the relationship among capacitance, dissipation factor and dielectric properties, we consider a plane-parallel condenser of vacuum capacitance, in which $C_0 = \epsilon_0 S/d$ (S and d are, respectively, the surface area of the plates and the thickness). If an a.c voltage $V = V_0 e^{i\omega t}$ is applied to this capacitor, a charge $Q = C_0 V$ appears. So the current becomes $I = i\omega C_0 V$. If the sample material is either slightly conducting or polar, the capacitor no longer perfect and the current is not exactly 90° out of phase with the voltage, since there is a small component of conduction GV in phase with the applied voltage [5]. In this case, the resultant current is: $I = (i\omega C + G)V$, where $G = \sigma S/d$, $C = \epsilon S/d$ and the current density is: $j = (i\omega\epsilon + \sigma)E$. These may be considered by introducing a complex permittivity $j = i\omega\epsilon^*E$, where $\epsilon^* = \epsilon - i\sigma/\omega$. The dissipation factor is such that:

$D = |\text{dissipative term/capacitive term}| = |\epsilon^* \text{ imaginary part}/\epsilon^* \text{ real part}| = \sigma/\omega\epsilon$.

As the temperature is increased, the complex permittivity of real part and imaginary part show the dispersion behavior with frequency change, which is attributed to the thermally

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Fig. 1. Dissipation factor D vs. temperature T curves with selected test frequencies for the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ ($X = 0.048$, $Y = 0.057$) epilayer.

activated process resulting from dipolar polarization effect. The thermally activated process usually has different relaxation time τ and the relaxation time τ will obey the relation: $\tau = \tau_0 \exp(E_a/k_B T)$.

2. Experiment

$\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ epilayers were grown on misoriented GaAs (001) substrates with dimension of $2 \text{ cm} \times 2 \text{ cm}$. The oxide on substrates was removed by heating the substrate to 580°C for about 30 s until a clear reflection high-energy electron diffraction (RHEED) pattern was observed. The EPI 40 cc low temperature cells were used for the evapo-

Fig. 2. Natural logarithm of the test frequency $\ln(f)$ vs. the reciprocal of the peak temperatures in the dissipation factor curves for the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ ($X = 0.048$, $Y = 0.057$) epilayer. The solid line is least-square fit for the data.

Fig. 3. Activation energy for carrier hopping as a function of the Mn and Te concentrations.

ration of the elemental solid source Zn, Te, and Se. For the Mn solid source, the EPI 40 cc standard temperature cell was used. During the growth of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$, the cell temperature of Zn was fixed at 300°C while the cell temperature of Se and Te ranged from 180 to 150°C and from 240 to 310°C , respectively, and the cell temperature for the Mn solid source was controlled around 700°C for the growth of low Mn concentration ($X < 0.05$) samples. The growth rate was about $0.1 \mu\text{m}$ per h. The Mn (x) and Te (y) concentrations were determined by the energy dispersive X-ray (EDX) measurement with detectivity of about 0.1% [6]. Capacitance (C) and dissipation factor (D) measurements were performed using a HP 428A LCR meter in a He Dewar with a Si diode as the temperature thermometer. Further details on the sample preparation and experimental apparatus were given elsewhere [1,7].

3. Results and discussion

A typical example of the dissipation factors (D) as a function of temperature (T) with selected test frequencies (f) for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ is shown in Fig. 1. At $T \sim 350 \text{ K}$, we observe a Debye-like relaxation in the dielectric response spectra. As the frequency increases, the peak around 350 K moves to high temperature, which suggests a temperature-dependent relaxation time. This behavior indicates that the relaxation process is thermally activated.

In order to see the temperature-dependence of the peak position, the logarithm of the test frequency versus the reciprocal of the peak temperature at the corresponding frequency is plotted in Fig. 2. It is clear that f and T obey the equation:

$$f = f_0 \exp(-E_a/k_B T), \quad (1)$$

where f_0 is a constant, k_B is the Boltzmann constant, and E_a is the activation energy. The thermal activation energy of the

Fig. 4. Capacitance vs. frequency for the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ epilayer for measurement temperatures of 180–460 K. ($X = 0.048$, $Y = 0.057$).

films can be determined from the slopes of $\ln(f)$ versus $1000/T$ plots as shown in Fig. 2. All our data can be fitted by Eq. (1) quite well. After the calculation, the values of activation energy were given in Fig. 3. As in the previous report, we believe that the Debye-like relaxation observed here is due to the existence of defects [8]. It is known that the defects responsible for carrier hopping can break the local symmetry and allow an electric dipole to exist [8]. The appearance of the electric dipole thus leads to the change of the dielectric response in the presence of an external electric field at different temperatures.

An interesting behavior observed in our dielectric studies can be obtained from Fig. 3. It is a 3D chart about Mn and Te concentration. We assign X component as Mn concentration, Y component as Te concentration, and Z component

Fig. 5. Arrhenius plot of the capacitance for the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ ($X = 0.048$, $Y = 0.057$) epilayers.

Fig. 6. The four-center model of the structure of the Zn vacancy defect V_{zn} , which locates at a site in the Zn sub lattice.

as the activation energy. We can see that there is a clear relationship between the activation energy and the Mn and Te concentration, i.e. the magnitude of the activation energy decreases with increasing Mn or Te concentration.

To explore the dielectric properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ epilayers further, capacitance measurements were taken over at different frequency and temperature as shown in Fig. 4. We can see that the capacitance (C) increases with decreasing test frequency (f). Carrier hopping on defects can attribute this effect to the effect of the charge redistribution [9,10]. At low-test frequencies, the charges on defects are more readily redistributed, such that defects closer to the positive side of the applied field become negatively charged while the defects closer to the negative side of the field become positively charged. This results in a screening of the field and an overall reduction in the electric field. Since capacitance is inversely proportional to the field, the reduction in field for a given applied voltage results in the increased capacitance observed as the frequency is lowered. As the frequency is increased, defects no longer have time to rearrange in response to the applied voltage, and thus the capacitance decreases. As expected and observed in Fig. 4, at a given frequency, when the temperature becomes higher, the capacitance value becomes larger [1]. Thus, we can say that higher the temperature the more effective the carrier hopping because of the increase in the thermal emission of charges. The activation energy (E_a) of the thermal emission can be obtained by the following equation:

$$1/f = K/T^2 \exp(E_a/k_B T), \quad (2)$$

where f is the test frequency, and K is proportionality constant. It is a modification of the equation derived by Stellwag et al. for capacitance recovery time [11]. The

thermal activation energy of the films was determined from the slopes of $\ln(T^2/f)$ versus $1000/T$. Fig. 5 shows a typical plot of the frequencies and the corresponding temperatures at which the capacitance is equal to 49.8 pF. Average activation energy was determined by averaging the E_a values obtained from frequency and temperature corresponding to different data of capacitance. It is found that the activation energies obtained from the dissipation factor and capacitance measurements are in nice agreement. Thus, our results indicate that the processes enumerated above are indeed thermally activated [1].

We now consider the relationship between Mn and Te concentration and the activation energy. In Fig. 3, it is found that when the value of Mn concentration is fixed, the activation energy decreases with increasing Te concentration. We interpret this behavior by the four-center model, which was first suggested by Fonger [12]. We consider the lattice of the ternary alloy $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$, and the defect center locates at the Zn vacancy as shown in Fig. 6. We can neglect the effect of Mn atom because its concentration is fixed at a small value. If the defect center is confined to the Zn vacancy, there are four different configurations arising from the occupation of Se or Te atoms on the four nearest-neighbor sites [1]. As we increase the concentration of Te atoms, the number of Te atoms occupying on the nearest-neighbor sites of the defect changes. Because the configurations of the nearest-neighbors of defects change with the increase of Te atoms, the behavior of defect is thus changed. Thus, the four-center model of the structure of the defects that differ with respect to the number of Te atoms appearing in them is used to account for the variation of activation energy. The gradual change of the activation energy is because of the relative broadband with only small differences in defect configurations, and the measured result is weighted by the relative concentrations of all defects involved in the center. Similar interpretation can also be applied to the situation in which the Te concentration is fixed and the Mn concentration is varied. Previously, the four-center model has been used to interpret the defect behaviors in GaAsP [13] and ZnCdTe [14], and etc. Here, we demonstrate that the four-center model can be applied to DMS compounds.

4. Conclusion

In conclusion, we have reported the dielectric properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}_{1-y}\text{Te}_y$ ($0.015 < X < 0.048$, $0.003 < Y < 0.103$) epilayers in the frequency and temperature range of 20–100 kHz and 180–460 K, respectively. A Debye relaxation behavior of the polarization has been observed. It is found that the relaxation is a thermally activated process and the activation energy decreases with increasing Mn and Te concentration. The activation energies obtained from the dissipation factor and capacitance measurements are in reasonable agreement. We use the four-center model to interpret the change of the activation energy with Mn or Te concentration. Our results demonstrate that dielectric studies can provide valuable information for the understanding of defect properties in DMS compounds.

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