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

H. M. Lin and Y. F. Chen^{a)}

Department of Physics, National Taiwan University, Taipei, Taiwan, Republic of China

J. L. Shen and W. C. Chou

Department of Physics, Chung Yuan Christian University, Chung-Li, Taiwan, Republic of China

(Received 25 September 2000; accepted for publication 21 December 2000)

We report on the dielectric properties of $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ alloys studied by capacitance and dissipation factor measurements at temperature $5\text{ K} < T < 475\text{ K}$ and frequency $20\text{ Hz} < f < 1\text{ MHz}$. A Debye-like relaxation of dielectric behavior has been observed, which is found to be a thermally activated process. The activation energies obtained from the capacitance and dissipation factor measurements are in excellent agreement. By means of our measurements, it is believed that the dielectric character of the carrier hopping among structural defects is responsible for the observed Debye relaxation. The relationship between the activation energy and Zn concentration has been established. The results are described by the four-center model, in which the number of Zn atoms appearing in the nearest-neighbor sites of a defect can have four possible configurations.

© 2001 American Institute of Physics. [DOI: 10.1063/1.1351006]

I. INTRODUCTION

Dilute magnetic semiconductors (DMS) are semiconductor alloys whose lattices are made up in part of substitutional magnetic atoms. Due to their unique magnetic, magneto-optical, electrical, and optical properties, DMS have attracted a great deal of attention.¹⁻³ For example, the energy gap and lattice parameter can be tuned by changing the composition. Because of the exchange interactions between local Mn moments and band electrons,⁴ many interesting phenomena have been discovered, such as extremely large Faraday rotation,⁵ giant negative magnetoresistance,⁶ and the magnetic polaron.⁷ Besides, under the external magnetic field, the properties of spin-glass transition,⁸ antiferromagnetic (AF) interaction, and magnon excitation⁹ have been observed. Among the studies of DMS, the reports of Mn-based DMS are abundant. The $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ alloys are the most extensively studied and probably best understood of the wide-gap DMS. It is found that the energy gap of this alloy system can be tuned from 1.6 to 2.7 eV at 10 K. It thus provides a potential candidate for the application of optoelectronic devices in the infrared and visible region. A quaternary $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ alloy system belongs to one of the DMS compounds. Compared with other DMS systems, its study is rather limited, and the physical property is relatively unknown. It is expected that quaternary compounds have more controlled parameters than ternary compounds and the potential of their applications are higher. For example, due to their wide range tuning of band gap and lattice constant, the quaternary crystals, $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$, are better candidates than the ternary compounds $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for the fabrication of optoelectrical devices and magnetic field sensors or for usage as the substrate for unstrained devices.

Even though many different techniques have been used to probe the physical properties of DMS compounds, the

dielectric study is absent for most DMS alloys. It is known that the dielectric properties of a solid are very sensitive to the local electric field distribution within the samples. Studies of the temperature and frequency dependence of dielectric properties can reveal useful information about structural changes, defect behaviors, and transport phenomena. In this article we present the measurements of capacitance and dielectric loss tangent of $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ alloys in a wide range of temperature and frequency. It is interesting that a Debye-like relaxation has been observed, which is attributed to the electron hopping among crystal defects. The relaxation is found to be thermally activated, and the obtained activation energy decreases with increasing Zn content. A microscopic structure of the defects based on the four-center model is proposed to explain the observed behavior.

II. EXPERIMENT

The alloys, $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$, were grown by temperature gradient solution growth with the temperature gradient close to $50^\circ\text{C}/\text{cm}$. The tellurium element was used as solvent, the anion (Te^{2-}) to cation (Cd^{2+} , Zn^{2+} , Mn^{2+}) molar ratio was 7 to 3. The large temperature gradient enables the impurities and excess Te to segregate to the higher temperature region. The crystal structure has been checked by x-ray measurement. The composition has been determined by energy dispersive x-ray spectroscopy. For all the crystals studied here, the Mn concentration is fixed at 0.05. The Zn composition is scanned from 0 to 0.95. The optical properties of the crystals have been studied by photoluminescence and reflectivity measurements. It is found that the band gaps of the studied $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystals range from red (1.6 eV) to green (2.3 eV). A detailed description of the crystal growth and the above-mentioned characterization have been reported elsewhere.¹⁰ Capacitance C and dissipation factor D were measured as function of temperature (4–500 K) and frequency (20 Hz–1 MHz) by using a HP 4284A LCR meter

^{a)}Electronic mail: yfchen@phys.ntu.edu.tw

FIG. 1. Dissipation factor D vs temperature T curves with selection test frequencies for the $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ ($x=0.4$ and $y=0.05$) crystal.

in a He dewar with a Si diode as the temperature thermometer. Similar apparatus have been described in detail in our previous reports.^{11,12} The measurements were performed on the dish-shaped samples with silver paint coated on two sides as the electrodes. Sensitivity to relative changes in capacitance was better than 10^{-5} . The complex dielectric permittivity $\varepsilon = \varepsilon' + \varepsilon''$ can be transformed from the capacitance C and the dissipation factor D as follows,¹³

$$\varepsilon' = Cd/A\varepsilon_0, \quad (1)$$

$$\varepsilon''/\varepsilon' = D. \quad (2)$$

III. RESULTS AND DISCUSSION

The dissipation factors as a function of temperature with selected test frequencies f for the $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystal with $x=0.4$ and $y=0.05$ are plotted in Fig. 1. A Debye-like relaxation in the dielectric response spectra has been observed. As the frequency increases, the peak shifts to a higher temperature, which suggests a temperature-dependent relaxation time.

In order to see the temperature dependence of the peak position, the logarithm of the test frequency $\ln f$ versus the reciprocal of the peak temperature at the corresponding frequency is plotted in Fig. 2. We can see that $\ln f$ and T obey the equation,¹⁴

$$f = f_0 \exp(-E/k_B T), \quad (3)$$

where f_0 is a constant, k_B is the Boltzmann constant, and E is the activation energy. This behavior indicates that the relaxation process is thermally activated. From the slope, the obtained activation energy is about 186 meV. The observation of a dielectric relaxation that requires a charge redistribution seems quite surprising for the system studied here. However, it is known that the defects responsible for carrier hopping can break the local symmetry and allow a dielectric dipole to exist.¹⁵ The appearance of the electric dipole thus leads to the change of the dielectric response in the presence of an external field at a different temperature.¹⁶

To explore the dielectric properties of $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystals further, capacitance measure-

FIG. 2. Natural logarithm of the test frequency $\ln f$ vs the reciprocal of the peak temperatures in the dissipation factor curves for the $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ ($x=0.4$ and $y=0.05$) crystal. The solid line is the least-squares fit for the data.

ments were taken over a frequency range of 20 Hz–100 kHz and a temperature range of 5–475 K. Shown in Fig. 3 is a typical variation of the capacitance of the $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ crystal with $x=0.2$ and $y=0.05$ as a function of test frequency and temperature. The capacitance decreases with increasing test frequency. This effect can be attributed to the effect of charge redistribution by mean carrier hopping on defects.^{17,18} At low frequency, the charge on the defects can be rapidly redistributed so that defects closer to the positive side of the applied field become negatively charged, while defects closer to the positive side of the applied field become positively charged. This leads to a screening of the field and an overall reduction in the electric field. Because capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased capacitance observed as the frequency is lowered. At high frequency, the defects no longer have enough time to rearrange in response to the applied voltage, hence the capacitance decreases. As expected and observed in Fig. 3, at a given frequency, the higher the temperature the more effective the carrier hopping because of the increase in the thermal emission of charges.

FIG. 3. Capacitance vs frequency for the $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ ($x=0.2$ and $y=0.05$) crystal for measurement temperatures of 130–160 K.

FIG. 4. Arrhenius plot of the capacitance for the $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ ($x=0.2$ and $y=0.05$) crystal.

From Fig. 3, the activation energy E_c of the carrier hopping can be determined by the following equation:

$$1/f = k/T^2 \exp(E_c/k_B T), \quad (4)$$

where f is the test frequency, and k is a proportionality constant. Equation (4) is a modification of an equation derived by Stellwag *et al.* for capacitance recovery time.¹⁹ Figure 4 shows a typical Arrhenius plot of the frequencies and corresponding temperature at which the capacitance is equal to 2.5 pF. The activation energy of defects can be obtained from the slope of an Arrhenius plot of $\ln(T^2 f^{-1})$ versus $1000/T$. An average activation energy was determined by averaging the E_c values obtained from frequency and temperature corresponding to three different data of capacitance. The activation energies obtained from the dissipation factor and capacitance measurement are in very good agreement.

Let us now consider the dependence of the activation energy on Zn content. We can clearly see that the magnitude of the activation energy decreases with the increase of Zn concentration in a monotonic fashion as shown in Fig. 5. To interpret this result we propose the four-center model first suggested by Fonger.²⁰ Considering an alloy $\text{A}_{1-x}\text{B}_x\text{C}$ with

FIG. 5. Activation energy (E) for carrier hopping as a function of Zn concentration (x). The Mn concentration ($y=0.05$) is fixed.

a zinc-blende structure, we assume the defect center locates at the C vacancy. If the defect wave function is sufficiently localized, the defect center is confined to the C vacancy and its nearest neighbors. There are four kinds of configurations of nearest-neighbor sites occupied by A or B atoms, as shown in Fig. 6. As the concentration of B atoms increases, the number of B atoms near the C vacancy increases. Because the configurations of the nearest-neighbors of defects change with the increase of B atoms, the behavior of defect is thus changed. The evidences of the four-center model have been observed in many alloys, such as GaAsP,²¹ GaInP,²² and ZnSSe.²³ For $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ alloys studied here, we can neglect the effect of the Mn atom because its concentration is fixed at a small value of 0.05. Therefore the four-center model of the structure of the defects that differ with respect to the number of Zn atoms appearing in them is used to account for the variation of activation energies. Because the number of Zn atoms appearing in the neighbors of the defect changes discretely, the properties of the defect should also reflect the same behavior. However, our results do not reveal a refined structure. Perhaps, it is because of relatively broad spectra with small differences in defect level, and the measured data is weighted by the relative concentration of all defects involved in the center. The similar defect behavior has also been observed in GaAsP (Ref. 24) and ZnCdTe (Ref. 25) by deep-level transient spectroscopy.

IV. CONCLUSION

In summary, the dielectric properties of $\text{Cd}_{1-x-y}\text{Zn}_x\text{Mn}_y\text{Te}$ alloys have been investigated. A thermally activated Debye-like relaxation in the dielectric response has been observed. This behavior is attributed to the charge redistribution by carrier hopping among defects. The variation of the activation energy of carrier hopping with Zn concentration is monotonic. This result is described by means of the four-center model, in which the number of Zn atoms appearing in the nearest-neighbor sites of a defect can have four possible configurations. Our results therefore dem-

FIG. 6. Four-center model of the structure of the defect D , which locates at a site in the C sublattice.

onstrate that dielectric study can provide valuable information for the understanding of defect behaviors in DMS compounds.

ACKNOWLEDGMENT

This work was partly supported the National Science Council of the Republic of China.

¹R. R. Galazka, *Inst. Phys. Conf. Ser.* **43**, 133 (1979).

²*Semimetal and Semiconductors*, edited by P. K. Willardson and A. C. Beer (Academic, New York, 1988), Vol. 25.

³J. K. Furdyna, *J. Appl. Phys.* **64**, R29 (1988).

⁴G. Dolling, T. M. Holden, and V. F. Sears, *J. Appl. Phys.* **53**, 7644 (1982).

⁵J. A. Gaj, R. R. Galazka, and M. Nawrocki, *Solid State Commun.* **25**, 193 (1978).

⁶M. Katsuno, N. Sawaki, T. Suzuki, and K. Hara, *Solid-State Electron.* **42**, 1557 (1998).

⁷R. Pittini, J. X. Shen, M. C. Debnath, I. Souma, M. Takahashi, and Y. Oka, *J. Appl. Phys.* **87**, 6454 (2000).

⁸S. B. Oseroff, *Phys. Rev. B* **25**, 6584 (1982).

⁹A. K. Ramdas, *J. Appl. Phys.* **53**, 7649 (1982).

¹⁰D. Y. Hong, Master thesis, Department of Physics, Chung-Yuan Christian University, Chung-Li, Taiwan, People's Republic of China, 1998.

¹¹J. W. Chen, J. C. Wang, and Y. F. Chen, *Physica C* **289**, 131 (1997).

¹²J. S. Su, J. C. Wang, and Y. F. Chen, *J. Appl. Phys.* **86**, 1630 (1999).

¹³J. C. Anderson, *Dielectrics* (Reinhold, New York, 1964).

¹⁴Yu. M. Poplavko, *Physic of Insulators* (Nauka, Kiev, 1980) (in Russian).

¹⁵A. Q. Jiang and Z. H. Chen, *Phys. Rev. B* **61**, 5835 (2000).

¹⁶G. B. Alers, B. Golding, A. R. Kortan, R. C. Haddon, and F. A. Theil, *Science* **257**, 511 (1992).

¹⁷P. W. Zukowski, S. B. Kantorow, D. Maczka, and V. F. Stelmakh, *Phys. Status Solidi A* **112**, 695 (1989).

¹⁸A. Vasudevan, S. Carin, M. R. Melloch, and E. S. Harmon, *Appl. Phys. Lett.* **73**, 671 (1998).

¹⁹T. B. Stellwag, M. R. Melloch, J. A. Copper, Jr., S. T. Sheppard, and D. Nolte, *J. Appl. Phys.* **71**, 4509 (1992).

²⁰W. H. Fonger, *Phys. Rev.* **137**, A1038 (1965).

²¹J. Samuelson, S. Nillsson, Z. G. Wang, and H. G. Grimmeiss, *Phys. Rev. Lett.* **53**, 1501 (1984).

²²A. Zunger, *Phys. Rev. Lett.* **54**, 849 (1985).

²³D. Block and R. T. Cox, *J. Lumin.* **24/25**, 167 (1981).

²⁴J. Criado, A. Gomez, E. Munoz, and E. Calleja, *Appl. Phys. Lett.* **49**, 1790 (1986).

²⁵A. Zerrai, G. Marrakchi, and G. Bremond, *J. Appl. Phys.* **87**, 4293 (2000).