Contributed paper

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Control of ferromagnetism in $Cd_{1-x}Mn_xTe$ quantum wells

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New structures aiming at controlling ferromagnetic properties of diluted magnetic semiconductors quantum wells are presented. The carrier density is monitored by applying voltage in p-i-n diode or adjusting a distance between quantum well and surface. Surface doping was successfully applied to obtain samples with CdMnTe quantum well with up to 9.3% Mn concentration.

Keywords: molecular beam epitaxy, quantum wells, magnetic materials, semiconducting II-VI materials.

1. Introduction

The ability to control the properties of magnetic materials would be highly desirable from fundamental and technological viewpoints, particularly in view of recent developments in magneto-electronics and spintronics. Diluted magnetic semiconductors (DMS), where ferromagnetic interactions are mediated through free carriers, are particularly attractive since they offer the possibility of modulation of magnetic properties by modulating the carrier density. The first demonstration has been performed by Ohno *et al*. [1] with III-V DMS layers inserted in a Schottky diode. They demonstrated that a gate voltage of ±125 V changes the Curie temperature by about 1 K in a field-effect transistor based on an (In,Mn)As thin layer. As compared to III-V magnetic semiconductors, Mn in II-VI semiconductors is isoelectronic and does not introduce any carriers. Hence, hole mediated ferromagnetic interactions can be induced by modulation doping of heterostructures.

2. Quantum wells inserted in p-i-n diodes

We have demonstrated [2,3] electric-field control of ferromagnetism in a $Cd_{0.96}Mn_{0.04}Te$ quantum well (QW). Our previous expertise in p-type [4] and n-type [5] modulation doping of tellurides makes it possible to successfully achieve the MBE growth of the semiconductor structure used in Ref. 2 and shown in Fig. 1(a). It consists of a $Cd_{0.65}Zn_{0.08}Mg_{0.27}Te$ p-i-n diode grown on a $Cd_{0.88}Zn_{0.12}Te$ substrate. The back barrier doped with aluminium (n-type) resided 320 nm away from the QW. A single, 10-nm thick, CdMnTe QW was introduced in the intrinsic layer 10 nm away from the p type (doped with nitrogen) contact layer. Without any applied voltage, a nominal hole concentration of 2×10^{11} cm^{-2} was present in the QW.

As shown in Fig. 1(b), recent improvement in the contact process allows us to obtain clear diode I-V characteristics and to reproducibly modify the carrier concentration in the well by applying a reverse bias.

The onset of ferromagnetism and the carrier concentration were determined optically: the experimental evidence for the presence or absence of a ferromagnetic transition was given by the spontaneous splitting, below a characteristic critical temperature T_c, of the photoluminescence (PL) line corresponding to the energy gap in the QW region. At the same time, a critical divergence of the field induced splitting at $T\rightarrow T_c+$ was observed. The value of the Moss-Burstein shift between the PL and photoluminescence excitation (PLE) was used to determine the hole density. The strong decrease in the Moss-Burstein shift, observed for a reverse bias, demonstrates the influence of the applied voltage on the hole concentration. Applying a reverse bias of –0.7 V led to a decrease in the hole concentration to zero in the QW. Figure 1(c) presents PL spectra collected for the p-i-n structure shown in Fig. 1(a) in the absence of an external magnetic field at various temperatures. Without applied voltage, the phase transition occurs below approximately 3 K in this sample. In contrast, at a reverse bias of –1 V no signature of ferromagnetism is observed in the PL spectra down to 1.5 K.

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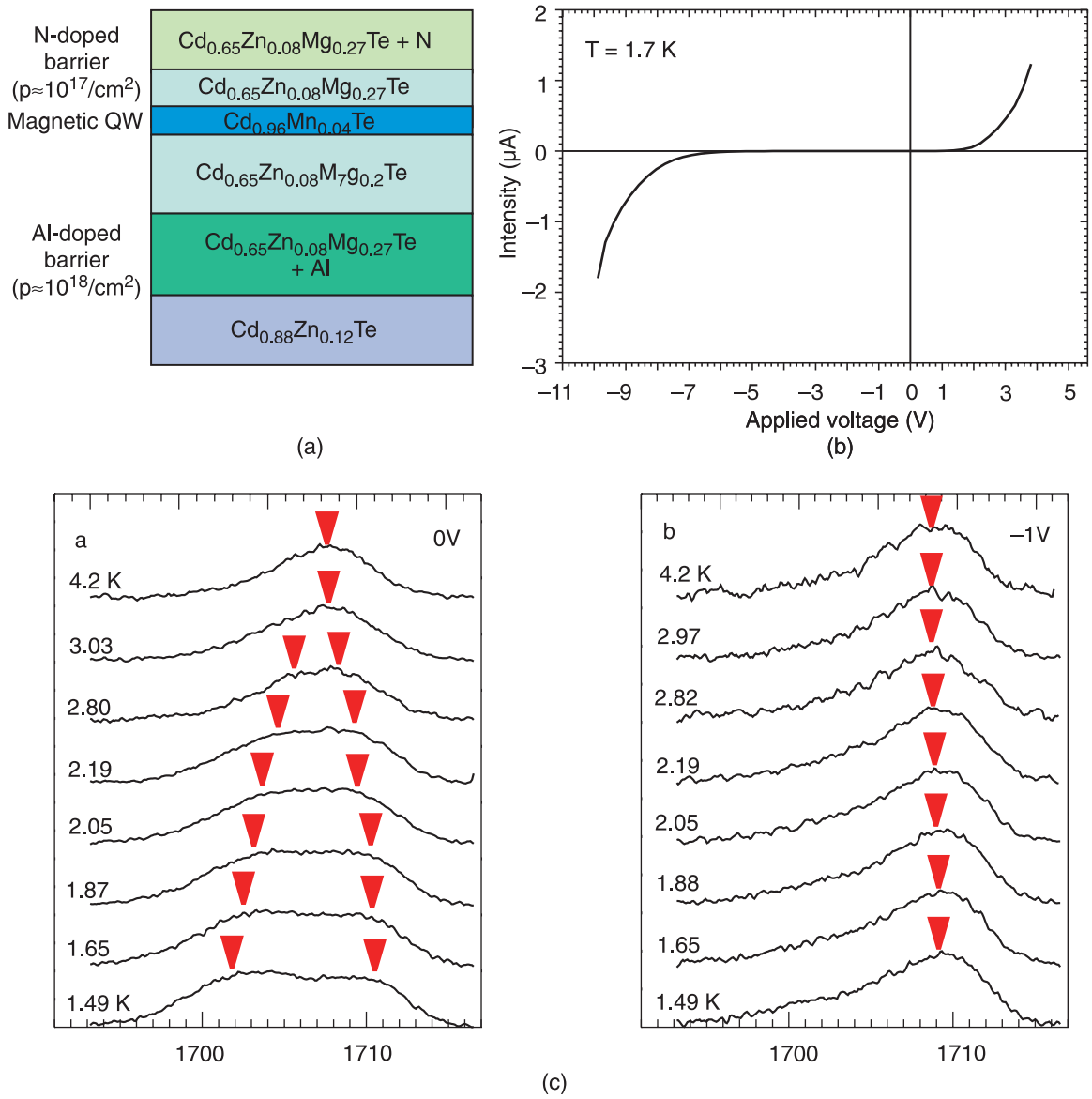

Fig. 1. Sketch of the p-i-n diode (a) and its I/V characteristics (b). Photoluminescence spectra of a $Cd_{0.96}Mn_{0.04}Te$ QW introduced in a CdZnMgTe diode measured at various temperatures (c): without bias (a) with a –1 V bias (b).

3. Doping from surface states

In the structure studied in Ref. 2 and shown in Fig. 1, N and Al were used for p and n type doping respectively. Nitrogen doped CdTe/CdZnMgTe heterostructures show a giant interdiffusion when the growth temperature is above 240°C [4]. Consequently, the structures were grown at low temperature so that the crystallographic quality is not fully optimised. We present here the observation of high carrier densities and carrier-induced ferromagnetism in CdMnTe QWs incorporated close to the surface in nominally undoped samples. The 10-nm thick CdMnTe QW was embedded in $Cd_{0.65}Zn_{0.08}Mg_{0.27}Te$ barriers. The sample structure is given in Fig. 2(a). Figure 2(b) gives an example of PL and PLE spectra for a sample containing 1.3% of Mn. The large Moss-Burstein (MB) shift indicates a large density of carriers in the QW. As shown in Fig. 2(c), for a QW with a Mn content of about 1%, varying the distance of the QW from the surface allows us to change the hole density (more than 2×10^{11} cm^{-2} for a QW located 25 nm below the surface). As shown in Fig. 2(c) a drop of the carrier density is observed on the samples with a very thin cap layer (below 20 nm).

For a cap layer of 25 nm and 4% of Mn in the QW, a ferromagnetic phase transition, with a critical temperature T_c of about 2.5 K, is deduced from the observation of the zero field splitting of the PL line when decreasing the temperature [Fig. 3(a)]. The experimental value of T_c can be obtained by tracing the position of the lower PL line as a function of temperature. As it can be seen in Fig. 3(b), the measured critical temperature (corresponding to the distinct knee) is very close to those measured on a nitrogen-doped sample with the same Mn content.

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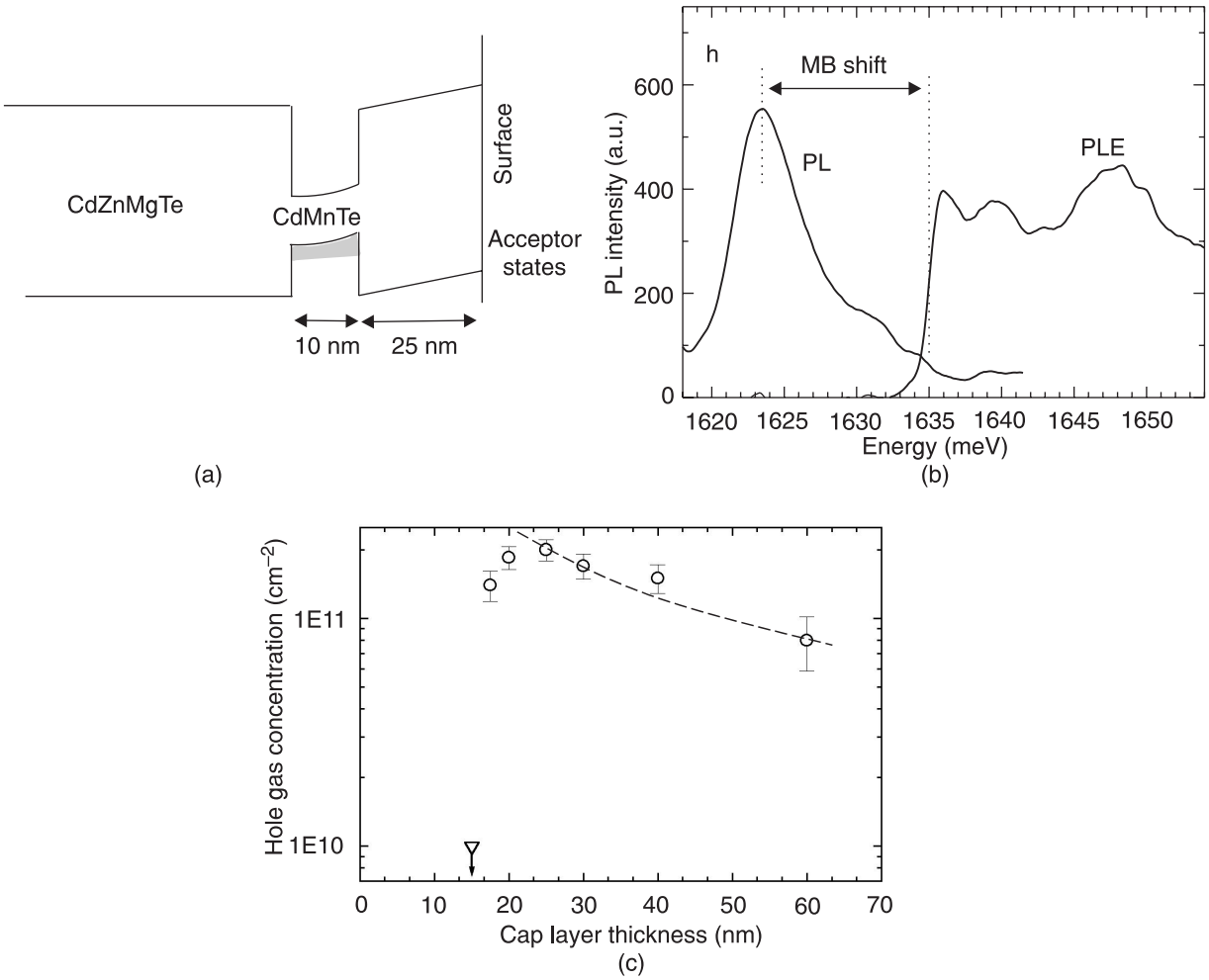

Fig. 2. Sample structure (a). PL and PLE spectra showing the Moss-Burstein shift (arrows) for a sample with a $Cd_{0.99}Mn_{0.01}Te$ QW (b). Hole density in 100 Å wide $Cd_{0.99}Mn_{0.01}Te$ QWs as a function of the cap layer thickness (c). The dashed line is the density expected from surface acceptor states at energy ΔE = 90 meV from the QW state.

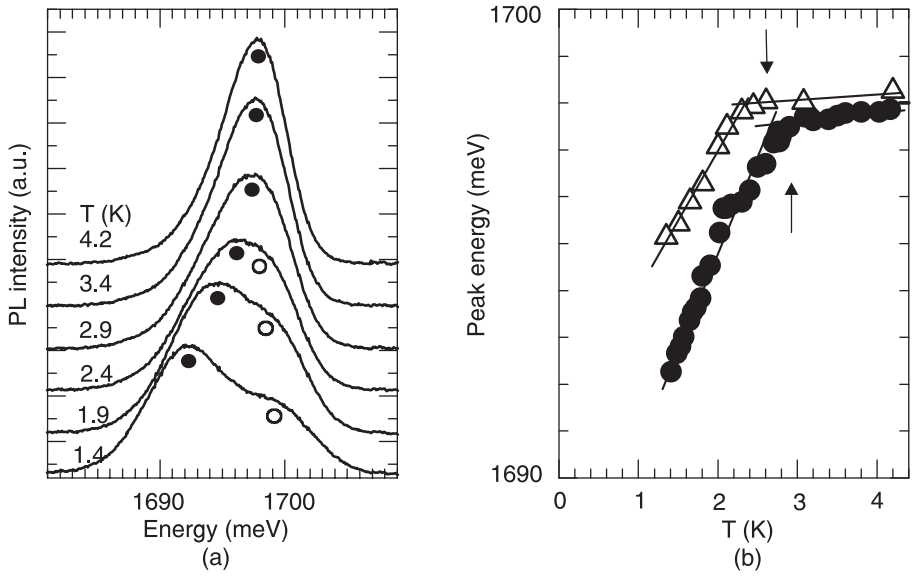

Fig. 3. Photoluminescence spectra at various temperatures of a CdMnTe QW embedded in CdZnMgTe barriers and located 25 nm away from the surface (a). Thermal dependence of the energy of the low-energy line (b). Surface doped sample (•) and nitrogen doped sample (Δ).

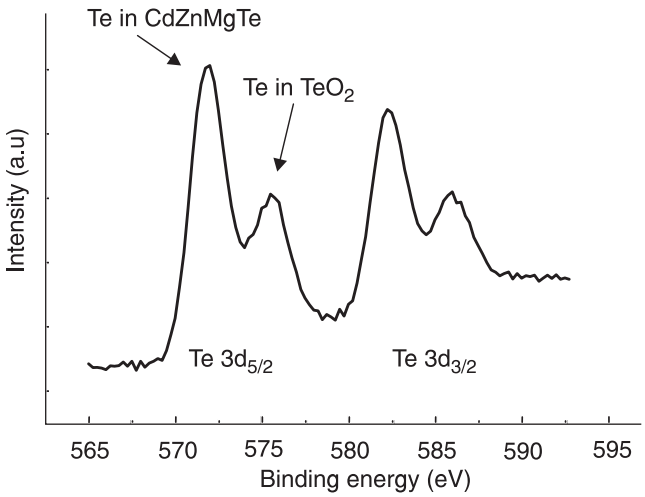

Fig. 4. XPS spectra of Te 3d core levels obtained for a $Cd_{0.65}Zn_{0.08}Mg_{0.27}Te$ (001) surface after 13 hours of oxidation.

The presence of a hole gas in the QW demonstrates the existence of surface states electrically active as acceptors, which we tentatively attribute to the formation of a surface oxide layer during exposure of the sample to the air. Indeed a negligible concentration of carriers was observed when we protected the sample from oxidation by depositing an amorphous Te layer. Similar observations have been made in different contexts. Yang *et al.* [6] using surface photovoltage spectroscopy observed an acceptor surface state on CdZnTe layers, attributed to the presence of TeO_2. In the same way, Wasik *et al.* [7] evidenced free electron trapping by surface defects in CdTe/CdMgTe heterostructures with QW lying close to the surface.

In order to get more information on the surface oxidation mechanisms as well as to control the oxidation of the surface (and consequently the hole density in the CdMnTe QW), we performed a detailed surface study of the oxidation kinetics of $Cd_{0.65}Zn_{0.08}Mg_{0.27}Te$ (001) by X-ray photoelectron spectroscopy (XPS).

Figure 4 presents the XPS spectrum of the $3d_{3/2}$ and $3d_{5/2}$ core levels of Te after oxidation for 13 hours at room temperature and oxygen pressure of 1 bar. The second lines, at higher binding energy which appears during oxidation correspond to the formation of TeO_2 [8].

Figure 5 presents the time evolution of the ratio of the TeO_2 line with respect to the total intensity (i.e., lines corresponding to CdZnMgTe and TeO_2). A ratio of about 0.25, obtained after 4 hours of oxygen exposure, allows us to estimate the formation of about 1 ML of oxide, assuming a photoelectron escape depth of 1.2 nm for the Te 3d core level [9]. Thus, the formation of a Te oxide is demonstrated but the oxidation of the surface is rather slow.

The evidence of Cd oxide formation is rather difficult due to the low difference in energy between the 3d lines corresponding to Cd-Te and Cd-O. However, as it can be seen in Fig. 5, after 10 hours of oxidation a broadening of the Cd $3d_{5/2}$ line occurs suggesting the presence of oxygen atoms bound to Cd ones [10].

Optical measurements have been performed on two samples exposed for respectively 4 hours and 90 hours to oxygen pressure and capped with a Pt layer. For the first sample no presence of carriers has been detected in the $Cd_{0.96}Mn_{0.04}Te$ QW indicating that the presence of a monolayer of TeO_2 on the surface is not a sufficient condition. In contrast, a hole density of 1×10^{11} cm^{-2} is obtained for the second sample, which exhibits the ferromagnetic transition.

Figure 6 shows an atomic force microscopy (AFM) image of the surface of a CdMnTe/CdZnMgTe sample exposed to air. It is worth noting the presence of islands on the surface (5–10 nm height).

Hence it appears that the oxidation mechanism of the surface is rather complex and the identification of the chemical nature of the acceptor surface states not straightforward. Anyway these preliminary results open the way to a control of the carrier density in the QWs by the control of the oxidation of the surface.

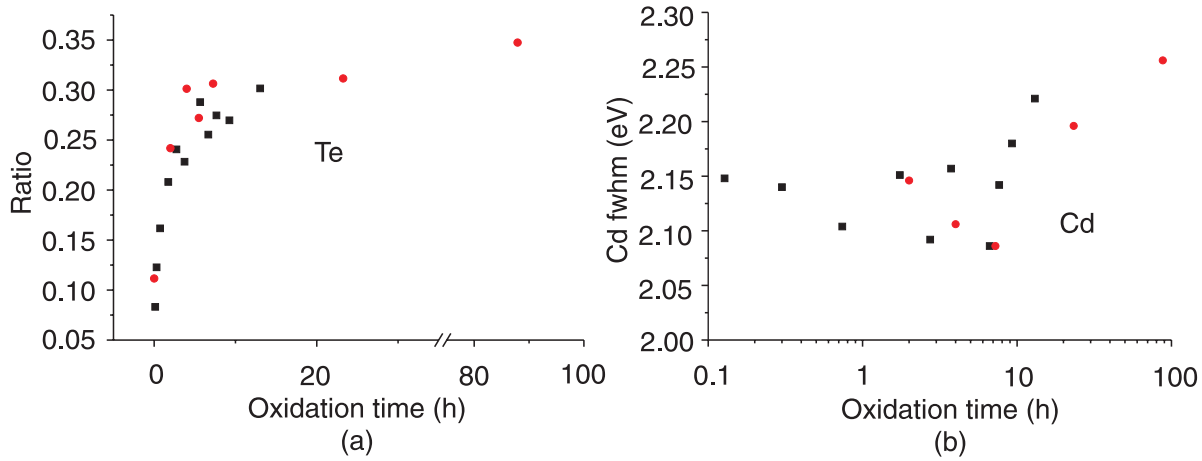

Fig. 5. Intensity of Te 3d peak corresponding to tellurium oxide relative to the total intensity of the Te peaks, as a function of oxidation time (a) and evolution of the FWHM of the $3d_{5/2}$ Cd peak as a function of oxidation time (b).

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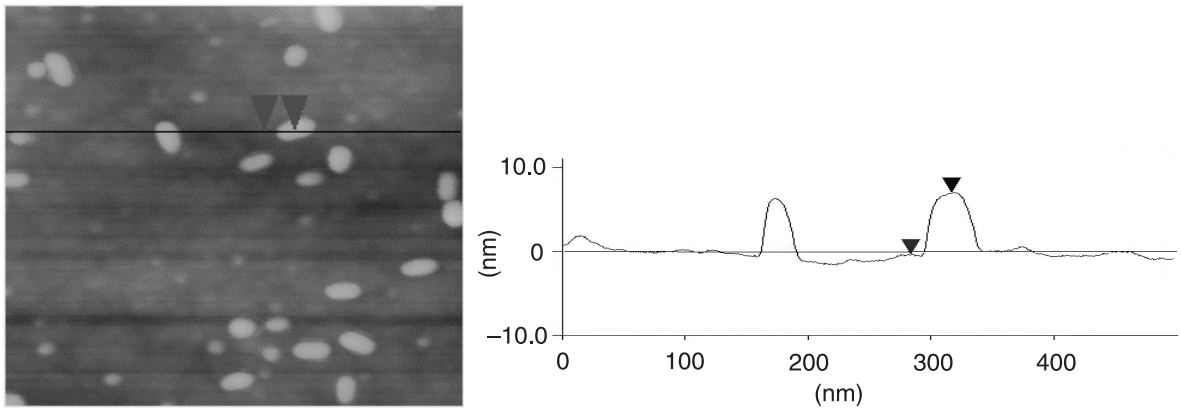

Fig. 6. AFM image (0.5×0.5 μm) of the $Cd_{0.65}Zn_{0.08}Mg_{0.27}Te$ surface after oxidation in air.

Doping with the surface states allows us to use higher growth temperatures (280°C instead of 220°C) and, consequently, make it possible to grow sample with a higher Mn content. Figure 7 illustrates the thermal dependence of the low energy peak position for three samples, doped by surface states, with different concentration of Mn in the QW. Remarkably a transition temperature of 5.5 K is measured for the sample with 9.3% Mn.

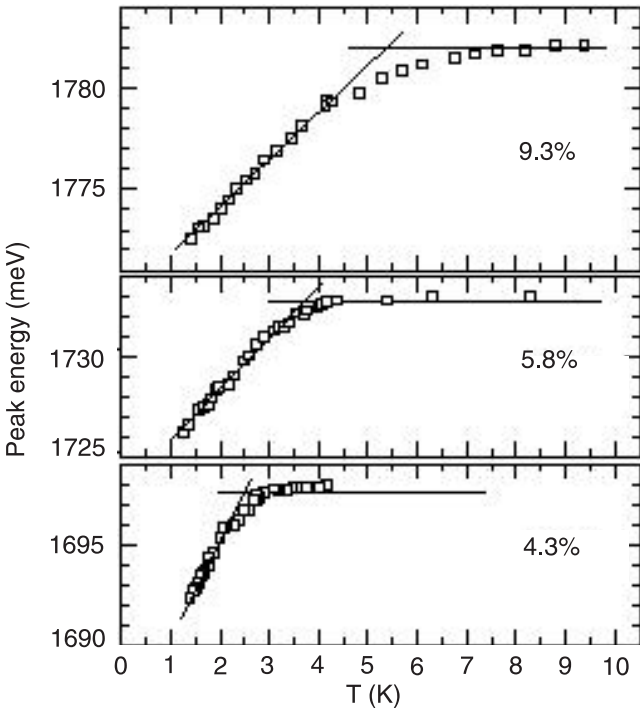

Fig. 7. Thermal dependence of low energy peak position for three samples with different Mn content. The knees indicate the transition temperature. Dashed lines present fits to the susceptibility measurements.

4. Conclusions

In summary we show that doping (and induced ferromagnetism) of a CdMnTe QW can be controlled by applying an electric-field to a p-i-n diode structure or by approaching the QW to the external surface. Doping from the surface states can be as effective as usual modulation doping with nitrogen. This last new way of doping increases the possibilities of controlling carrier-induced ferromagnetism in quantum wells. Particularly, eventually, a preliminary study of the surface has been presented, but the understanding of the mechanism responsible for surface doping need further experiments.

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References

1. H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, and K. Ohtani, "Electric field control of ferromagnetism", *Nature* **408**, 944–946 (2000).
2. H. Boukari, M. Bertolini, J. Cibert, D. Ferrand, Y. Genuist, S. Tatarenko, P. Kossacki, J.A. Gaj, and T. Dietl, "Light and electric field control of ferromagnetism in CdMnTe based quantum wells", *Phys. Stat. Sol.* **229**, 737–739 (2002).
3. H. Boukari, P. Kossacki, M. Bertolini, D. Ferrand, J. Cibert, S. Tatarenko, A. Wasiela, J.A. Gaj, and T. Dietl, "Light and electric field control of ferromagnetism in magnetic quantum structures", *Phys. Rev. Lett.* **88**, 207204-1-207204-4 (2002).
4. A. Arnoult, J. Cibert, S. Tatarenko, and A. Wasiela, "Interdiffusion mechanisms in CdTe/CdMgZnTe:N modulation doped heterostructures", *J. Appl. Phys.* **87**, 3777–3784 (2000).
5. A. Arnoult, D. Ferrand, V. Huard, J. Cibert, C. Grattepain, K. Saminadayar, C. Bourgognon, A. Wasiela, and S. Tatarenko, "n and p type modulation doping of Te related semimagnetic II-VI heterostructures", *J. Cryst. Growth* **201/202**, 715–718 (1999).
6. J. Yang, Y. Zidon, and Y. Shapira, "Alloy composition and electronic structure of CdZnTe by surface voltage spectroscopy", *J. Appl. Phys.* **91**, 703–707 (2002).

7. D. Wasik, M. Baj, J. Siwiec-Matuszyk, T. Wojtowicz, E. Janik, and G. Karczewski, "Parasitic conduction phenomena in modulation doped CdTe/CdMgTe:I heterostructures grown on GaAs substrates", *J. Appl. Phys.* **91**, 753–756 (2002).
8. T.B. Wu, J.S. Chen, C.D. Chiang, Y.M. Pang, and S.J. Yang, "Study of polished and etched surfaces of polar (111) CdTe by x-ray photoelectron spectroscopy and grazing incidence x-ray diffraction", *J. Appl. Phys.* **71**, 5212–5216 (1992).
9. M.A. George, M. Azoulay, H.N. Jayatirtha, A. Burger, W.E. Collins, and E. Silberman, "X-ray photoelectron spectroscopy and atomic force microscopy characterization of the effects of etching ZnCdTe surfaces", *Surf. Science* **296**, 231–240 (1993).
10. D.P. Masson, D.J. Lockwood, and M.J. Graham, "Thermal oxide on CdSe", *J. Appl. Phys.* **82**, 1632–1639 (1997).

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