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Post-annealing effect on the electronic structure of Mn atoms in $Ga_{1-x}Mn_xAs$ probed by resonant inelastic x-ray scattering

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Abstract

The electronic structure of as-grown and post-annealed $Ga_{1-x}Mn_xAs$ epilayers ($x \approx 0.055$) has been investigated using resonant inelastic x-ray scattering. Mn $L_{2,3}$ x-ray emission spectra show that the integral intensity ratio of Mn L_2 to L_3 emission lines increases with annealing temperature and comes close to that of manganese oxide. The oxygen K-emission/absorption spectra of post-annealed $Ga_{0.945}Mn_{0.055}As$ show 1.5–3.0 times higher degree of oxidation on the film surface than that of the as-grown sample. These experimental findings are attributed to the diffusion of Mn impurity atoms from interstitial positions in the GaAs host lattice to the surface where they are passivated by oxygen.

The Mn-doped GaAs system has received considerable attention recently as a promising III–V diluted magnetic semiconductor (DMS) for spintronic technology. This system can possess a Curie temperature (T_C) as high as 160 K [1, 2]. According to recent research [3, 4], the holes induced by the substitution of divalent Mn for trivalent Ga mediate the ferromagnetic interaction between Mn dopants in $Ga_{1-x}Mn_xAs$. It is expected that the nominal hole concentration should be equal to the number of Mn atoms per unit volume. However, the measured hole concentration is found to be much less, by at least a factor of ∼3. Most theories regarding ferromagnetism in DMSs attribute a suppressed T_C to the reduction of hole concentrations [3]. This hole concentration deficiency is subject to some scrutiny and it has been variously attributed to either As in the form of antisites and interstitials [5] or to Mn interstitials [6, 7]. There have been attempts to raise the value of T_C by increasing the

hole concentration through post-annealing at low temperatures that are close to the growth temperature. This method resulted in an increase of T_C up to 160 K. It has been suggested that the observed changes in T_C can be attributed to the diffusion of high mobile Mn interstitials towards the surface [1, 6, 8]. Therefore, it is of great importance for practical applications to clearly understand the role that the Mn dopants play in determining the magnetic and electronic properties of $Ga_{1-x}Mn_xAs$.

In this study, we employ resonant inelastic x-ray scattering to probe which sites the Mn dopants occupy in $Ga_{1-x}Mn_xAs$. This technique also allows us to monitor how the Mn dopants redistribute themselves after undergoing low-temperature (LT) annealing.

The Mn-doped GaAs samples were grown at a substrate temperature of 250 °C using an LT molecular-beam epitaxy (LT-MBE) method. 100 nm thick $Ga_{1-x}Mn_xAs$ samples ($x \approx 0.055$) were grown onto epi-ready GaAs(001) substrates. The stoichiometric ratio of Mn dopants in the samples (5.5%) was verified using high-resolution x-ray diffraction (HR-XRD). The magnetic ordering temperature for the as-grown samples were determined to be between 50 and 62 K, by using a combination of SQUID magnetometry and transport measurements. Samples were then annealed under a dry flowing N_2 environment in a tube furnace for one hour, with an annealing temperature (T_A) of either 200 or 290 °C. Further details of the growth and characterization of $Ga_{1-x}Mn_xAs$ are reported elsewhere [9].

The transport measurements, as well as structural measurements, on the effects of annealing are similar to those reported by others [1, 2], with an initial decrease in resistivity, and a corresponding increase in T_C and hole concentration, as defects such as Mn interstitials are removed. The resistivities then increase, with a corresponding decrease in T_C and hole concentration, above some optimal annealing temperature [10]. The XRD measurements show that the peaks associated with $Ga_{1-x}Mn_xAs$ epilayers shift slightly towards GaAs when the samples are annealed at the temperatures considered. Although this indicates a relative decrease in the lattice constant of $Ga_{1-x}Mn_xAs$ samples, quantitative comparison from HR-XRD measurements alone is difficult [11].

The x-ray emission spectroscopy (XES) measurements were carried out at beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. Non-resonant oxygen Kα emission spectra (2p $\rightarrow$ 1s transition) and resonantly excited manganese $L_{2,3}$ (3d4s $\rightarrow$ 2p transition) emission spectra were recorded at room temperature (RT). All measured spectra were normalized to the number of photons falling on the sample, which is monitored by a highly transparent gold mesh. O 1s and Mn 2p x-ray absorption spectra (XAS) were measured in partial fluorescence yield (PFY) mode.

Oxygen K-emission and absorption spectra of as-grown and annealed $Ga_{0.945}Mn_{0.055}As$ samples are presented in figure 1. The spectra of as-grown samples indicate the presence of oxygen on the surface of GaAs. As shown in figure 1, annealing the samples increases the oxygen content 1.5–3.0 times the base level using annealing temperatures of 200 and 290 °C, respectively.

Mn 2p XAS spectra for as-grown and annealed $Ga_{0.945}Mn_{0.055}As$ samples are shown in figure 2. The features around 640 and 651 eV correspond to the L_3 ($2p_{3/2} \rightarrow 3d4s$) and L_2 ($2p_{1/2} \rightarrow 3d4s$) levels. The fine structure of Mn L_3 XAS is absent for the as-grown sample and arises for the two annealed samples (features *A* and *B*). The fine structure of the annealed samples resembles the features shown by MnO and therefore these changes can be attributed to the formation of manganese oxide on the surface of $Ga_{0.945}Mn_{0.055}As$ during annealing [12].

The Mn $L_{2,3}$ XES spectra of the $Ga_{0.945}Mn_{0.055}As$ films (as-grown, annealed at 200 °C, and annealed at 290 °C) measured at different excitation energies (*b* and *c* in figure 2) are presented in figures 3(a) and (b). The two main bands located around 638 and 645 eV can be assigned as normal Mn L_3 (3d4s $\rightarrow$ $2p_{3/2}$ transition) and Mn L_2 (3d4s $\rightarrow$ $2p_{1/2}$ transition) emission lines,

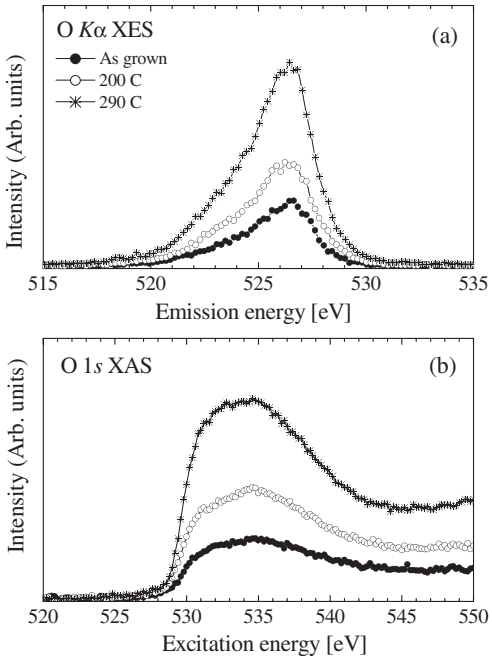

Figure 1. Oxygen K-emission spectra (a) and 1s absorption spectra (b) of as-grown and post-annealed $Ga_{0.945}Mn_{0.055}As$ films.

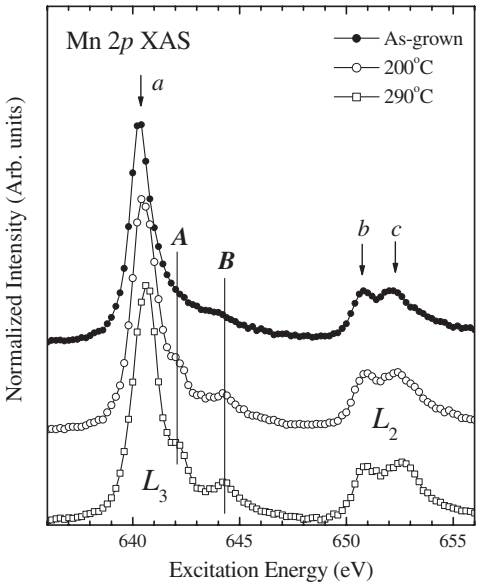

Figure 2. Mn 2p XAS spectra of as-grown and post-annealed $Ga_{0.945}Mn_{0.055}As$ films.

respectively. Their energy separation corresponds exactly to spin–orbital splitting of Mn 2p and does not change with the excitation energy used. We note that the integral intensity ratio of Mn L_2 to L_3 emission lines $[I(L_2)/I(L_3)]$ of the as-grown sample excited at the L_2 threshold is

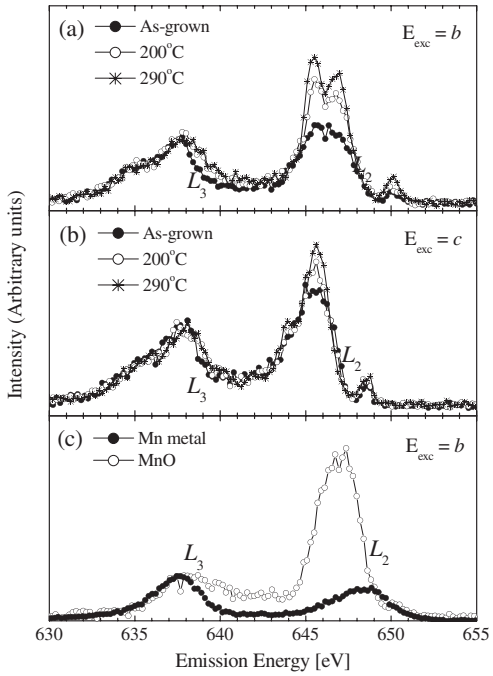

Figure 3. Resonant inelastic x-ray scattering spectra of as-grown and post-annealed $Ga_{0.945}Mn_{0.055}As$ films at the Mn L_3 (a) and Mn L_2 (b) edges. The resonant spectra of reference samples (MnO and Mn metal) at the Mn L_3 edge are shown in figure (c) for comparison.

smaller than that of samples annealed at 200 °C and 290 °C. The differences in the resonantly excited Mn $L_{2,3}$ XES spectra of our samples reflect the changes in the site distribution of the Mn impurity atoms; this is discussed below.

The L_2 and L_3 x-ray emission from 3d elements corresponds to x-ray transitions from (occupied) 3d4s valence states to $2p_{1/2}$ and $2p_{3/2}$ core vacancies. In solids, the relative intensity ratio of L_2 to L_3 XES lines, $I(L_2)/I(L_3)$, is influenced by radiationless $L_2L_3M_{4,5}$ Coster–Kronig (CK) transitions. Generally, CK transitions partially depopulate the L_2 core holes of the system when radiationless electron transitions from the L_3 to the L_2 level occur before the emission process can take place. In this case the transition energy can be released via emission of 3d Auger electrons. The probability for this process is strongly enhanced in condensed matter systems because a screening of intra-atomic electron interactions in solids leads to a decrease in the energy difference between the initial and final states of the radiationless CK process. This effect becomes particularly prominent in metals [13]. This tendency is illustrated by comparing the XES spectra of metallic Mn and dielectric MnO. Figure 3(c) shows Mn $L_{2,3}$ XES spectra of metallic Mn and MnO samples resonantly excited at the L_2 absorption edge. Since L_2 resonant excitation gives rise to the preferential formation of L_2 holes (relative to L_3 holes). Mn $L_{2,3}$ XES spectrum of an insulating MnO exhibits a much higher L_2 emission line than L_3 line. However, the $I(L_2)/I(L_3)$ intensity ratio is significantly reduced for metallic Mn due to the radiationless Coster–Kronig (CK) transitions.

Comparing the spectra of $Ga_{0.945}Mn_{0.055}As$ with the spectra of Mn and MnO reference samples, we find that the Mn $L_{2,3}$ XES spectra of the sample annealed at 290 °C are very similar to that of MnO. This similarity is not surprising if we assume that both types of Mn impurity atoms are present in the as-grown sample, occupying both substitutional and interstitial sites.

This is contrasted with the samples that underwent an annealing step. According to other reports [1, 6], the diffusion activation energy of Mn interstitial atoms is relatively lower than that of other defects such as substitutional Mn atoms and As antisites. This means that the annealing can initiate the significant diffusion of highly mobile Mn interstitials to the surface, where they then become passivated by oxygen, forming MnO. Therefore the sample that has undergone annealing at a higher temperature (290 °C versus 200 °C) exhibits more similarity to MnO than the sample annealed at 200 °C. It should be noted that x-ray transitions in the x-ray emission process occur within the Mn atom and thus the corresponding XES spectra are determined mainly by the first coordination sphere of the excited atom. On the other hand, the Mn $L_{2,3}$ XES spectra of the as-grown sample are more similar to the XES spectra of Mn metal than to those of MnO due to Mn–Mn bonds between Mn substituted atoms and Mn interstitials. However, as seen in figure 3, the intensity ratio $I(L_2)/I(L_3)$ gradually increases with increase in the annealing temperature. This gives direct evidence that LT annealing causes the diffusion of Mn interstitials to the surface and thus removes the Mn–Mn bonds in the samples. We therefore attribute the changes in the distribution sites of Mn in $Ga_{0.945}Mn_{0.055}As$ films to diffusion of Mn atoms to the surface and their passivation by oxygen after LT annealing. This is in accordance with the increased oxygen content in annealed $Ga_{0.945}Mn_{0.055}As$ samples shown in figure 1. Since such changes in local ordering depend on the annealing temperature and are not accompanied by the formation of additional phases, only a chemically sensitive local-probe method like XES provides an efficient analysis.

We have shown that x-ray fluorescence measurements can be used to probe the local ordering changes in Mn-doped GaAs films, and its dependence on annealing temperature. By monitoring the intensity ratio $I(L_2)/I(L_3)$ of resonantly excited Mn $L_{2,3}$ emission spectra and the intensity of oxygen K-emission and absorption spectra, it is found that low-temperature annealing induces the diffusion of Mn interstitials to the surface and their passivation by oxygen there.

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