Curie temperature and carrier concentration gradients in MBE grown Ga$_{1-x}$Mn$_x$As layers

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We report on detailed investigations of the electronic and magnetic properties of ferromagnetic Ga$_{1-x}$Mn$_x$As layers, which have been fabricated by low-temperature molecular-beam epitaxy. Superconducting quantum interference device measurements reveal a decrease of the Curie temperature from the surface to the Ga$_{1-x}$Mn$_x$As/GaAs interface. While high resolution x-ray diffraction clearly shows a homogeneous Mn distribution, a pronounced decrease of the carrier concentration from the surface towards the Ga$_{1-x}$Mn$_x$As/GaAs interface has been found by Raman spectroscopy as well as electrochemical capacitance-voltage profiling. The gradient in Curie temperature seems to be a general feature of Ga$_{1-x}$Mn$_x$As layers grown at low-temperature. Possible explanations are discussed.

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Over the past years, the field of spin electronics, which aims at the use of the spin of carriers for electronic devices, is of growing interest. A combination of conventional semiconductors with magnetism, where both band gap engineering as well as magnetic engineering could be realized, would be very desirable. One material under investigation is the semimagnetic semiconductor Ga$_{1-x}$Mn$_x$As, which can be made ferromagnetic with Curie temperatures $T_C$ as high as 150 K as reported so far. This ferromagnetism is attributed to be due to the exchange interaction between holes and the magnetic moment of Manganese, and hence $T_C$ strongly depends on both the Mn content $x$ and the concentration $p$ of holes:

$$T_C \propto x \times p^{1/3}$$

(1)

The high density of holes in Ga$_{1-x}$Mn$_x$As originates from the incorporation of Mn itself, which acts as an acceptor on Ga lattice sites and in addition provides the magnetic moments.

In this work, we have investigated the magnetic and electronic properties of ferromagnetic Ga$_{1-x}$Mn$_x$As layers by superconducting quantum interference device (SQUID) measurements, electrochemical capacitance-voltage (ECV) profiling as well as Raman measurements. A pronounced vertical gradient of the carrier concentration was found, which consequently leads to a gradient of the ferromagnetic coupling and therefore to a variation in $T_C$ from the surface towards the Ga$_{1-x}$Mn$_x$As/GaAs interface. Our results indicate that this obviously is a general aspect of low-temperature molecular-beam epitaxy (MBE) grown Ga$_{1-x}$Mn$_x$As layers and has to be taken into account in the analysis of their physical properties.

Ga$_{1-x}$Mn$_x$As thin films were grown by low-temperature MBE at a substrate temperature of $T_S = 250 \, ^\circ C$. For providing As$_4$ a valved As cracker cell was used in the noncracking mode with a As/Ga beam equivalent pressure ratio of 30, whereas for Ga and Mn conventional Knudsen cells were used. The growth procedure was as follows: A 100-nm-thick GaAs buffer layer was grown at high temperature (585 °C) on a semi-insulating GaAs(001) substrate, then the sample was cooled down during a growth break of 45 min to $T_S = 250 \, ^\circ C$, and finally the Ga$_{1-x}$Mn$_x$As layer was grown. Below we will discuss our findings on the basis of the Ga$_{1-x}$Mn$_x$As layer with $x = 5.1\%$, measured by HRXRD, where the effects observed in all samples under investigation are most pronounced. After the growth the sample was etched by wet chemical etching to 100 nm and 140 nm etch depth, respectively. The unetched and etched pieces of the same sample were analyzed by SQUID magnetization measurements, Raman spectroscopy as well as ECV profiling.

SQUID magnetization measurements show a decrease in $T_C$ from 90 K in the as-grown sample to 55 K in the sample with 140 nm etch depth (Fig. 1). This corroborates results obtained from ferromagnetic resonance measurements which have already pointed to the fact that there is a gradient in the magnetic properties. The inset of Fig. 1 shows the decrease in measured $T_C$ versus etch depth.

According to Eq. (1), a change in Curie temperature
can be caused either by a gradient in Mn content $x$ or by a gradient in the carrier concentration $p$.

To check for a gradient in Mn distribution, we performed HRXRD measurements. A Mn gradient should affect the shape of the HRXRD curve. In Fig. 2 the measured HRXRD spectrum of the as-grown sample is shown as well as a simulation, assuming a homogeneous Mn content $x = 5.1\%$. The position of the Ga$_{1-x}$Mn$_x$As peak as well as the full width half maximum (FWHM) of the measurement agrees nearly perfectly with the simulation. Therefore, a gradient in Mn content as the origin of the observed decrease in $T_C$ can be ruled out. The Ga$_{1-x}$Mn$_x$As layers are homogeneous in terms of lattice constant, and are of high quality, as can also be seen by the pronounced thickness fringes, indicating a sharp Ga$_{1-x}$Mn$_x$As/GaAs interface.

To check for a vertical gradient in hole concentration $p$ across the Ga$_{1-x}$Mn$_x$As layer, ECV profiling is a suitable method overcoming the complications that arise from the anomalous Hall effect which affects standard transport studies of carrier concentration in conducting ferromagnetic materials. ECV profiling measurements using a BioRad PN4400 with a 0.2M NaOH:EDTA solution as the electrolyte were performed on an as-grown piece of the sample, which was used for Raman and SQUID measurements. Indeed, the ECV profile also shows a decrease in hole concentration by a factor of 2 from $8 \times 10^{20}$cm$^{-3}$ to $4 \times 10^{20}$cm$^{-3}$ from the surface to the Ga$_{1-x}$Mn$_x$As/GaAs interface (Fig. 3).

To confirm the result of ECV profiling we have performed Raman spectroscopy measurements. The Raman signals of the unetched and the 140-nm-etched sample are compared in Fig. 3. As discussed in detail in Ref. 4 the high hole concentration in Ga$_{1-x}$Mn$_x$As leads to the formation of a coupled mode of the longitudinal optical (LO) phonon and the hole plasmon. With increasing hole concentration the frequency of this coupled mode shifts from the frequency of the LO phonon to that of the transverse optical (TO) phonon. Figure 3 clearly reveals that the coupled mode in the etched sample is shifted towards the LO-phonon frequency if compared to the unetched sample, indicating a reduced hole concentration.

As a result, we have detected a vertical gradient in the hole concentration, leading to a vertical gradient in the Curie temperature. We suggest that this gradient is generally occurring in Ga$_{1-x}$Mn$_x$As layers grown by LT-MBE, as will become clear from the discussion below, and has to be taken into account when measuring the properties of such samples.

Meanwhile it is well known that post-growth annealing of Ga$_{1-x}$Mn$_x$As at temperatures near the growth temperature can change the magnetic behaviour of these
layers. The origin of this annealing effect is obviously due to changes in the point defect structure of the low temperature grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. E.g., diffusion of As antisites and the rearrangement of Mn at interstitial sites or a combination of both are under discussion. The main point is that these effects are observed during annealing at temperatures near or even below the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ growth temperature.

If annealing near or even at the growth temperature changes the defect structure, then this should also happen during growth. Whether this annealing leads to a higher or lower Curie temperature depends, however, on the particular nature of point defects in the structure. The exact microscopic processes are very complex and still unclear.

In addition to this annealing effect, a change of surface temperature during growth can be also a source of vertical gradients. When Mn is incorporated into GaAs, the effective bandgap $E_g$ shrinks and the free carrier concentration goes up $(10^{20}\text{cm}^{-3}$ or higher). As a consequence, the absorption of infrared light coming from the hot effusion cells in the MBE system increases and thus the surface temperature gradually rises. An increased growth temperature again can change the point defect structure of the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ substantially, which in turn affects the magnetic and electrical properties.

The observed vertical gradient in $T_C$ can also explain the unusual magnetization curves $M(T)$ of as-grown samples measured by our group (Fig. 1), but also by others. The $M(T)$ curves of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layers usually do not show a simple Curie-Weiss behaviour. This can be explained by the superposition of various $M(T)$ curves from parts of the layer with different Curie temperature. A detailed investigation of magnetization curves will be published elsewhere.

In conclusion we have shown that as-grown $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layers potentially show a vertical gradient in carrier concentration and therefore in their magnetic properties. We suggest that this is due to the intrinsic high point defect density, which leads to high diffusion constants of point defects already at growth temperatures. Even though the vertical gradient in Curie temperature depends on the particular growth process used, it is suggested to be a general and intrinsic property of low-temperature $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ layers, which can lead to a severe misinterpretation of the data if not taken into account properly.

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