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Systematic investigation on the influence of the As_4 flux on the magnetic property of (In,Cr)As quantum dots

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Abstract – We study the structure, optical and magnetic characteristics of self-assembled (In,Cr)As diluted magnetic semiconductor quantum dots as a function of the As_4 flux. Increasing the surface energy by increasing the As_4 pressure leads to a smaller number of larger dots for a higher As_4 flux. The remanent magnetization measured at 5 K also increases with increasing As_4 flux, which is attributed to the enhancement of the effective Cr content due to the As_4-rich condition. We explore the possibility of tailoring magnetism by controlling the As_4/In flux ratio without changing the Cr concentration. Furthermore, extremely low-density QDs have also been successfully grown.

Introduction. – Self-assembled III–V semiconductor quantum dots (QDs) (such as InAs QDs grown on GaAs) using the Stranski-Krastranow growth mode by molecular-beam epitaxy (MBE) have been studied extensively for nanoelectronic and optoelectronic applications due to the discrete density of states originated from three-dimensional quantum confinement [1–3]. On the other hand, a magnetic nanodot array (such as Co, Fe) has been proposed as one of the solutions to overcome the superparamagnetic effect and large transition noise of thin-film media for use in future generations of magnetic recording media [4,5]. Diluted magnetic semiconductor QDs, combining the materials mentioned above, may be suitable for a versatile control of the number of carriers, spin, and the effects of quantum confinement which could lead to improved optical, transport, and magnetic properties, and could hold particular promise as building blocks for spintronic devices [6]. Recently, our group reported the growth of self-assembled (In,Cr)As diluted magnetic semiconductor QDs with the Curie temperature (T_C) above 300 K [7], making (In,Cr)As QDs a promising candidate for high-temperature operation of spin-based devices.

For the growth of InAs QDs, it is well known that the size, shape, and density of the islands are essential parameters in determining their electronic, optical properties [8,9]. On the other hand, the geometrical and structural features of the islands critically depend on the growth conditions. Therefore, detailed information about the effects of various growth parameters is the prerequisite for realizing electronically and optically efficient nanostructures. Reports in the literature about the influence of the As_4 flux on InAs QDs differ significantly [8,10–12]. This may be related to the fact that the beam equivalent pressure values given in different reports are basically not comparable because they are machine dependent. Only a qualitative discussion of the observed phenomena is possible. The As_4 flux was discussed in connection with the mobility of atomic species on the surface [8], surface energy [13], indium desorption [10], and indium segregation efficiency [11].

In this study, we report a detailed investigation on the effects of the As_4 flux on the growth kinetics, structure, optical and magnetic characteristics of (In,Cr)As QDs grown on GaAs (001) substrates by MBE, particularly with regard to size evolution, QD density and the possibility of tailoring magnetism through the As_4 flux.

Experiments. – A series of (In,Cr)As QDs (samples A, B, C, D) with various V/III flux ratios (22, 45, 83, 190) were grown on GaAs (001) substrates using a solid source MBE system (V80 MARKI) equipped

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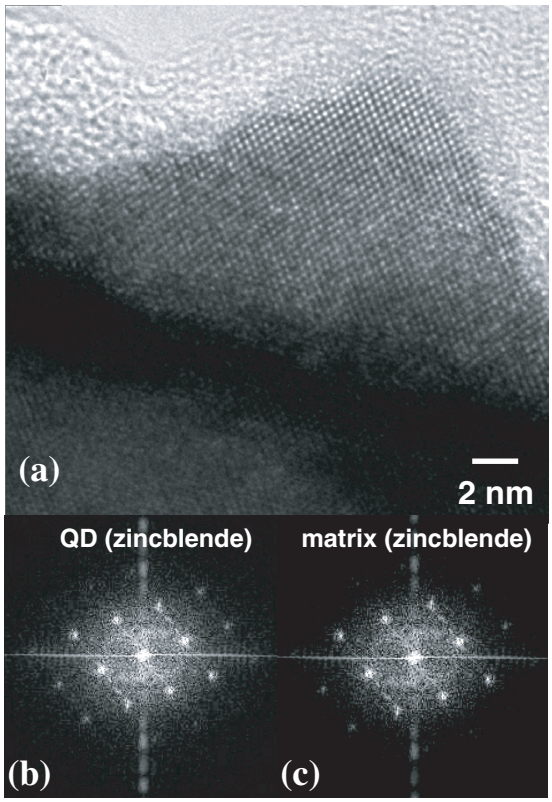

Fig. 1: (a) Cross-sectional HRTEM image of sample D, (b) the FFT picture of the QD and (c) the FFT pattern of the GaAs matrix.

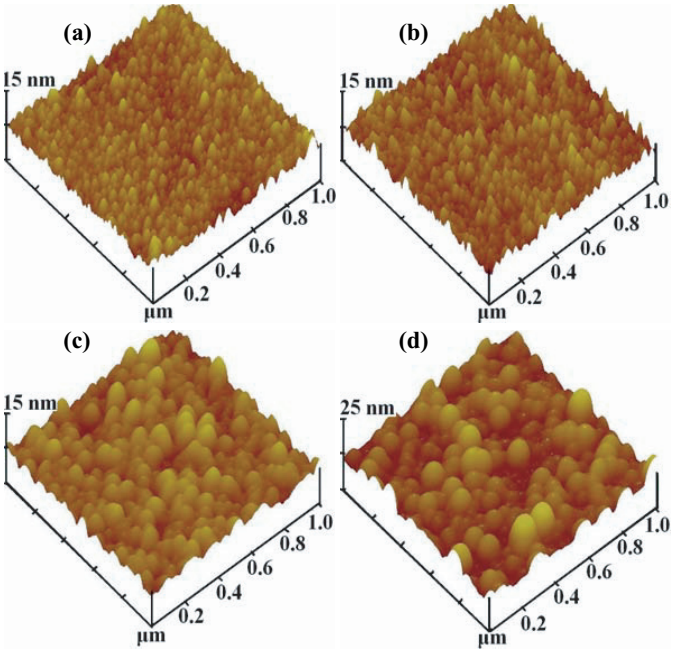

Fig. 2: (a)–(d) Three-dimensional AFM images of the same area of $1 \times 1\,\mu\text{m}^2$ for samples A, B, C and D.

with a 12 keV reflection high-energy electron diffraction (RHEED). Temperature was measured by a thermocouple (W/Re-W/Re (5%–26%)) which is in contact with the substrate holder. The oxide layer was desorbed at 580 °C, and then a 100 nm GaAs buffer layer was first grown at 560 °C to smoothen the surface. After deposition of the InAs wetting layer at 250 °C, the Cr cell was opened for the growth of a 6 MLs (In,Cr)As QDs. During the growth of the (In,Cr)As QDs, the growth rate was 0.048 ML/s and the Cr/In beam equivalent pressure ratio was 0.05 which was calculated according to relative pressure values on the ion gauge. The amount of deposited (In,Cr)As was determined from RHEED pattern, wherein the appearance of so-called chevrons in the $[1\bar{1}0]$ azimuth corresponded to a critical coverage of 1.7 MLs. On the other hand, we measured the oscillations period of the RHEED pattern intensity to determine the growth rate of InAs. Then according to the data we can calculate the deposition thickness at this growth temperature for a total deposition time. The growth process was monitored *in situ* with RHEED. Initially, a (2×4) streaky pattern was observed during the growth of the GaAs buffer layer at high temperature, while it changed to streaky (1×1) at the initial growth of the InAs wetting layer. After completion of the wetting layer and growth break, the pattern changed to spotty (1×1). During and after the growth of the (In,Cr)As QDs, the spots grew larger and eventually transformed to round shape, suggesting the formation of (In,Cr)As dots with a zincblende crystalline structure.

Results and discussion. – The detailed determination of the microstructure and of the crystallographic phase of the (In,Cr)As QDs was performed by cross-sectional high-resolution transmission electron microscopy (HRTEM) measurements. Figure 1(a) shows the cross-sectional HRTEM image of the (In,Cr)As QDs in the sample D in the [110]-direction. From it we can see that the dot maintains a zincblende crystalline structure and is near pyramidal in shape. Two-dimensional electron diffraction patterns were obtained from the GaAs matrix and the QD by fast Fourier transform (FFT). The diffraction patterns indicate that both are zincblende, as shown in figs. 1(b) and (c). Neither evidence of a hexagonal NiAs-type CrAs cluster was observed from the HRTEM image, nor was a second lattice structure detected by FFT under the limitation of the resolution of this measurement system.

The nanoscale variation of the Cr composition within a single QD layer is resolved by energy dispersive spectroscopy analysis. We found that the majority of Cr dopants reside in the dots with Cr concentration in the range of 2–7 at.%, varying perceptibly from dot to dot, and nearly no Cr atoms can be detected in the GaAs matrix. These results show that we obtained zincblende (In,Cr)As QDs.

Figure 2 shows the three-dimensional (3D) atomic force microscopy (AFM) images of samples A, B, C, and D. A most notable difference among these layers is the high

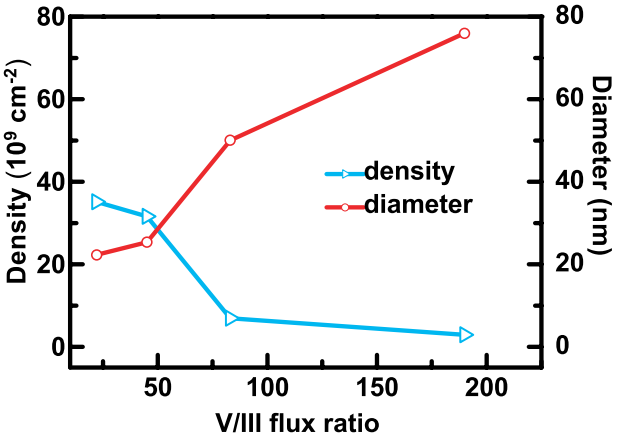

Fig. 3: Density and diameter for (In,Cr)As QDs as a function of the V/III flux ratio.

density and small size of (In,Cr)As dots for the layer grown at lower As_4 flux as seen in figs. 2(a) and (b). While the density of (In,Cr)As dots grown at higher As_4 flux is significantly reduced, leading to a more uniform size distribution and larger coalescent (In,Cr)As dots (shown in figs. 2(c) and (d)).

Figure 3 shows the average diameter and density of (In,Cr)As dots as a function of the V/III flux ratio. The average diameter of dots is about 22.29, 25.34, 50.03 and 75.99 nm, respectively. The dot density is approximately 3.51×10^{10}, 3.16×10^{10}, 6.94×10^{9} and $2.91 \times 10^{9}\,\mathrm{cm}^{-2}$, respectively. Increasing the As_4/In flux ratio from 22 to 190 brings about the increase in size of dots and the decrease in density of dots. The change of the island size distribution indicates that the mobility of surface atoms is not limited by the impinging atomic fluxes in the present range of As_4 pressure. Thus, we speculate that the present As_4 pressures are comparatively low. This is consistent with the observation of Ledentsov *et al.* [13], who found a growing QD size with increasing As_4 pressure in the range of low arsenic pressures, while they found a size reduction of QDs with increasing As_4 pressure in the range of high As_4 pressures.

Figures 4(a), (b), (c) and (d) show the distribution of quantum dot heights (from AFM images) for samples A, B, C and D. The maximal height of dot increases with increasing As_4 pressure. In addition, a low percent of higher QDs starts to appear for the layer grown under high As_4 pressure. Figures 4(e), (f), (g) and (h) present the photoluminescence (PL) spectra for samples A, B, C and D. The broad spectra indicate wide size distributions. To visualize the size increase, we utilized Gaussian fitting curves showing three dominant size distribution modes labeled S, M and L, corresponding to their respective relative sizes (small, medium, and large). We found that increasing the As_4 pressure leads to an increase in the QD size and a high percent of medium and large quantum dots.

Next, we discuss the possible origin of the size and density evolution of (In,Cr)As QDs based on the four

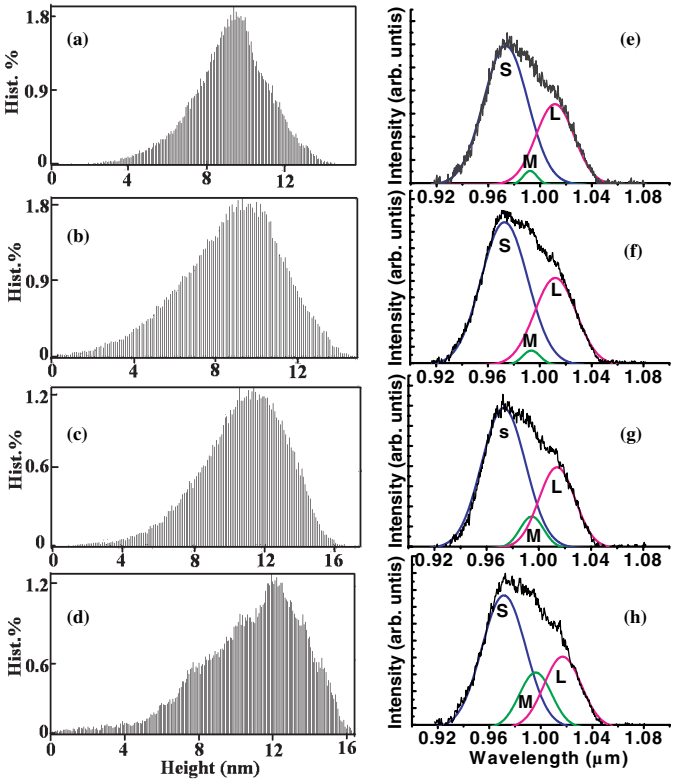

Fig. 4: Panels (a), (b), (c) and (d) show the distribution of quantum dot heights; panels (e), (f), (g) and (h) present the PL spectra for samples A, B, C and D. Gaussian fitting curves show three dominant size distribution modes which are labeled S, M and L.

mechanisms mentioned above: the mobility of atomic species on the surface, surface energy, indium desorption, and indium segregation efficiency. Within prevailing views, the decrease in the island density may be qualitatively reconciled as a consequence of the enhanced indium surface migration [14]. However, if analyzed in terms of cation migration, the arsenic pressure dependence would require an enhanced indium migration with increasing arsenic pressure at the low temperatures. This would be counter to the general belief that increased anion pressure inhibits cation migration. Thus we need to seek a description of island formation involving kinetic processes beyond only cation migration. It has been previously reported that an increased arsenic to cation steady-state coverage during growth gives rise to an increase of surface excess strain energy which leads to an enhancement of the intraplanar and upwards interplanar cation migration rate [15]. Therefore, we deduce that the observed decrease in the (In,Cr)As island density and the concomitant increase in the average lateral size of the islands are more relevant to the increasing surface energy with increasing As_4 pressure. Enhanced indium desorption at lower As_4 fluxes with its corresponding influence on the QD size is another possible explanation. However, it is assumed not to be relevant for the substrate temperature used for the samples discussed in this article. In addition, indium

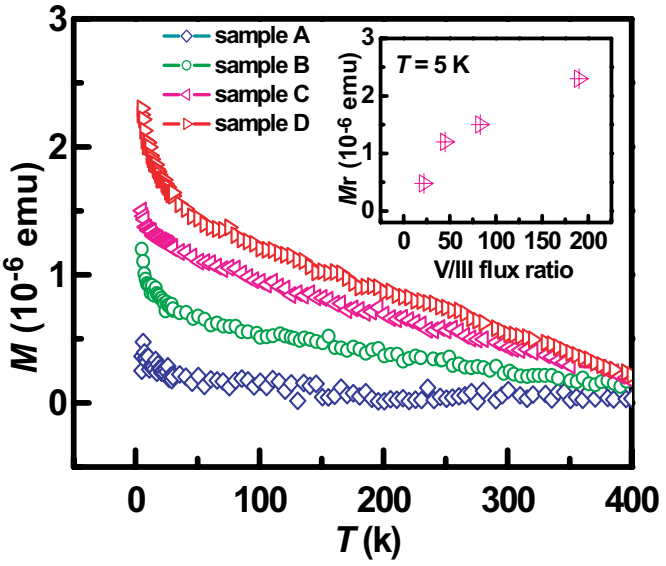

Fig. 5: Temperature dependence of the remanent magnetization of samples A, B, C and D. Inset: remanent magnetization measured at 5 K as a function of the V/III flux ratio.

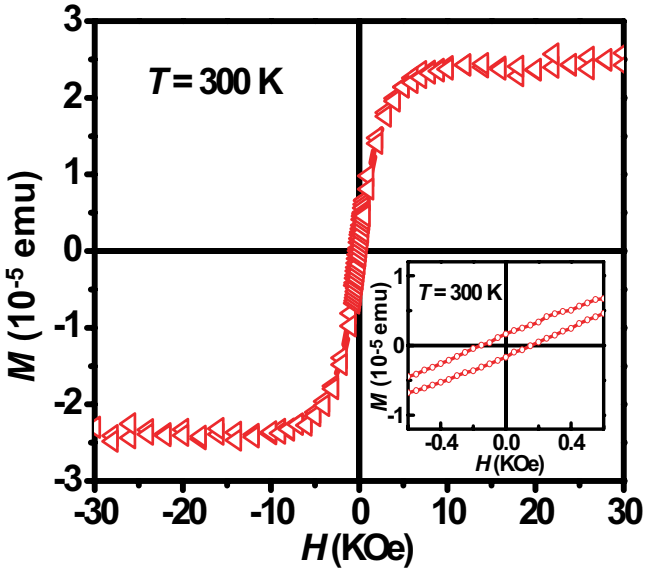

Fig. 6: *M*-*H* curve for the sample D measured at 300 K. The low field range is shown in the inset.

segregation efficiency and the corresponding effects on the size and density cannot be completely excluded because they were shown to depend on the beam equivalent pressure ratio value in ref. [11].

The temperature dependence of the remnant magnetization was measured by a superconducting quantum interference device (SQUID) in order to determine the T_C of the samples. A fixed procedure was employed as follows. A magnetic field of 1 T was applied along the [110] crystal direction to magnetize samples at 5 K, and then it was reduced to 0 T. Afterwards, the remnant magnetization was recorded when temperature gradually changed from 5 K to 400 K. From fig. 5 we can see that the T_C of (In,Cr)As QDs is higher than 300 K even though the remnant magnetization is relatively small. It should be noted that the T_C of the present (In,Cr)As QDs is much higher than those of III-V diluted magnetic thin films. According to the model presented by Lyu and Moon [16], the enhancement of the hybridization strength between the quantum-confined carriers in quantum dots and the itinerant carriers in the semiconductor valence band may render carrier transferring easier, leading to an increased T_C.

As mentioned above, while measuring the temperature dependence of the remnant magnetization, all the samples experienced the same magnetization history. Therefore, we may get useful information about As_4 pressure effects on the magnetic properties from analyzing the As_4/In flux ratio dependences of their remnant magnetizations. As shown in the inset of fig. 5, with increasing As_4 flux, the remnant magnetization increases. This result is consistent with the change of the size of the quantum dots. As we know, in the (Ga,Mn)As diluted magnetic semiconductor grown under As_4-rich condition, Mn prefers to substitute the Ga site. As the growth conditions become less As_4-rich, the formation energy of interstitial Mn becomes competitive with that of the substitutional Mn [17]. We speculate that a similar mechanism also works for Cr-doped QDs. At high V/III ratios, Cr is more likely incorporated into a lattice position, where it acts as an acceptor, than into an interstitial site, where it behaves as a compensating donor and can form antiferromagnetically ordered Cr_I-Cr_{In} pairs by occupying positions adjacent to Cr_{In}. That is to say, the effective substitution of the Cr concentration increases with the increase of the As_4 flux, which enhances the magnetization moment. Thus, it is possible to tailor the magnetism of QDs by controlling the As_4/In flux ratio without changing the Cr concentration.

The magnetic-field dependence of in-plane magnetization at 300 K was also measured. All the samples show ferromagnetic hysteresis. Figure 6 selectively shows the the magnetic hysteresis of the sample D. The diamagnetic contribution of the GaAs substrate and of the buffer layer has been subtracted from the data. The curve demonstrates a clear hysteretic loop (as can be seen in the inset of fig. 6), confirming the existence of ferromagnetism at room temperature.

We also want to report that extremely low-density magnetic QDs have been successfully grown at high substrate temperature and large As_4 pressure. The samples were grown at 520 °C. The nominal Cr concentration is 0.3%, and As/In flux ratios are 60 and 85. Figure 7 shows the AFM images of the two samples. Particularly, we only observe three QDs in the range of 1 μm^2, as shown in fig. 7(b). This result indicates that the self-assembled growth of a single quantum dot with only one or two magnetic ions is feasible. It provides the possibility to probe and manipulate the spin state

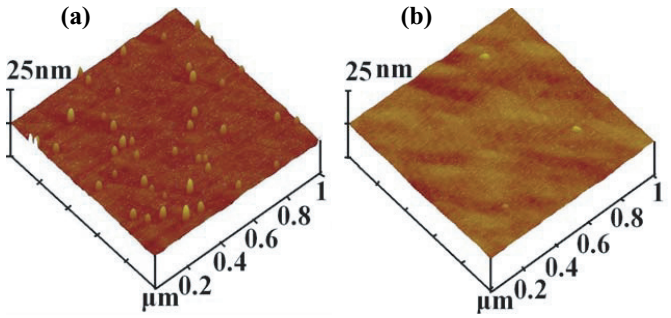

Fig. 7: AFM images of samples grown at high temperature with an As/In flux ratio of 60 (a) and 85 (b).

in such a system, which is a primary building block of nanoscopic spin-based devices in particular for the realization of quantum bits. Further experiments and theoretical insights are in progress to sort out these issues.

In summary, we systematically investigated on the influence of the As_4 flux on the structure, optical and magnetic properties of (In,Cr)As diluted magnetic semiconductor quantum dots. The microstructure analysis reveals that the (In,Cr)As QDs have a zincblende structure. It is evident that with increasing As_4 pressure, the dot size increases, while the density decreases. High As_4 pressure leads to the enhancement of the surface energy, which is the main reason. Furthermore, the remanent magnetization measured at 5 K also increases with increasing As_4/In flux ratio, which is attributed to the enhancement of the effective Cr content due to the As_4-rich condition. Extremely low-density magnetic QDs were also reported. Therefore, it is possible to tailor magnetism by controlling the As_4/In flux ratio without changing the Cr concentration.

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