In-Situ Growth of MnAs nanocrystals in Si studied by Transmission Electron Microscopy

Johannes Biskupek, Andrey Chuvilin, Ute Kaiser,
Oliver Picht* and Werner Wesch*

Electron Microscopy Group of Materials Science, Ulm University, Germany
*Institute of Solid State Physics, Friedrich Schiller University, Jena, Germany
johannes.biskupek@uni-ulm.de

MOTIVATION

Ferromagnetic nanocrystals inside a semi-conducting matrix [1] are aimed to the development of new devices in the field of spintronics e.g. data information storage and high sensitive magnetic sensors [2]. It was already shown that high dose ion implantations [Ge, Sm, Co, Mn, As] into SiC or Si followed by rapid thermal annealing lead to the formation of embedded nanocrystals [3,4]. In the case of Co-implantation it was shown that the nanocrystals are ferromagnetic [5]. In this work we study the growth process in-situ from the situation after ion implantation to the finally grown nanocrystals.

Experimental

Mn (200 keV) and As (270keV) ions (total dose $2*10^{16}cm^{-2}$) have been co-implanted at 350°C into [100]-Si wafers.
Proper TEM sample preparation is a essential task because the process has to be studied in cross-sectional view and the sample must withstand temperatures up to 1000°C. Cross-section TEM samples have been prepared using the following methods and techniques:
Sandwiches were glued together with ceramic based glue instead of common epoxy (for high temperature treatment) and were put into special Ti-grids. The thin TEM sample was made by using mechanical grinding, dimpling and polishing, followed by low angle Ar-ion etching. Plasma cleaning of the final sample has been used to remove any residual hydro carbons from the sample surface to avoid contamination during heating.
In-situ TEM investigations were carried out using a Philips CM20 microscope together with a Gatan heating stage sample holder (specified to 1000°C). HRTEM, EFTEM and STEM-tomography investigations were carried out using a Cs-corrected FEI Titan 80-300 operating at close to zero Cs. The Titan is equipped with a Gatan Tridiem energy filter.

In-Situ Annealing

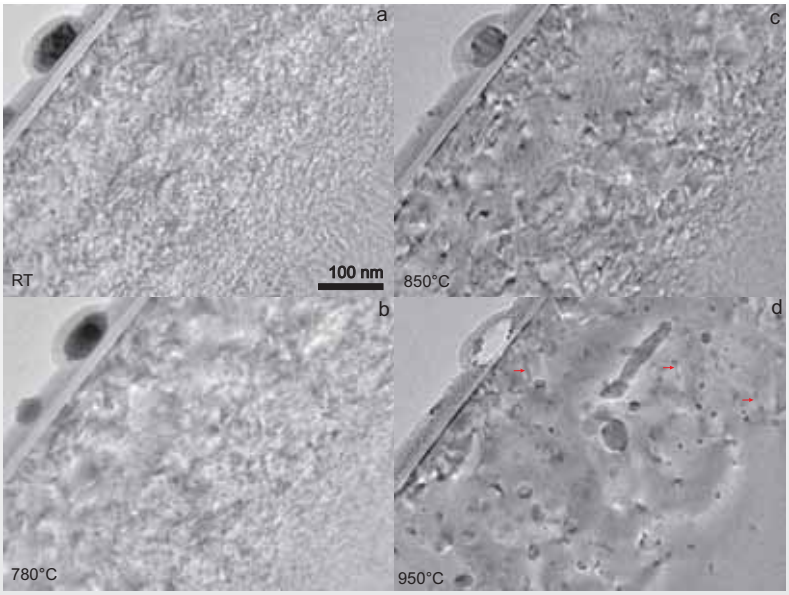

Figure1. In-situ annealing

Fig.1a shows the sample after ion implantation. The heavily damaged area of about 300nm due to the ion irradiation can be seen in the bright-field image.
Fig.1b: The sample at about 780°C. The implantation defects are starting to disappear. At this temperature nanocystals are not yet forming.
Fig. 1c: At 850°C small nanocrystals are beginning to form which can be seen due to Bragg and absorption contrast.
Fig. 1d: The sample is shown after cooling down from 950°C back to RT. Large Nanocrystals have been formed. The matrix does not contain the implantation defects as in Fig.a. Interstitial dislocations (red arrows) are visible at the end of the nanocrystals [6]. (The particle top-left in Fig1.a-d close to the surface is some residual ceramic glue.)

Fig. 2a: A different sample region than in Fig.1. The formation of voids starts to appear at 850°C (some examples are marked with red arrows).
Fig. 2b: The sample shown at the same temperature 5min later. The voids are now filled with nanocrystals.

Apparently matrix and foreign atoms become very mobile. Voids start to grow. Foreign atoms glide along dislocations that end at voids and start to fill the voids (marked with the red arrows in Fig.2) [6].
In the top-right corner an enlargement of the boxed area is shown, demonstrating the filling of the voids with nanocrystals

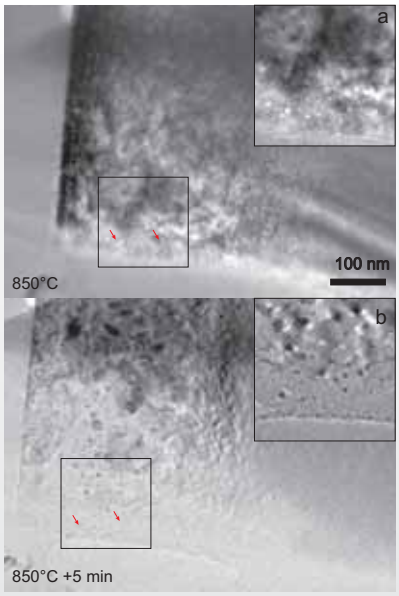

Figure 2. In-situ annealing,

Nanocrystal structure

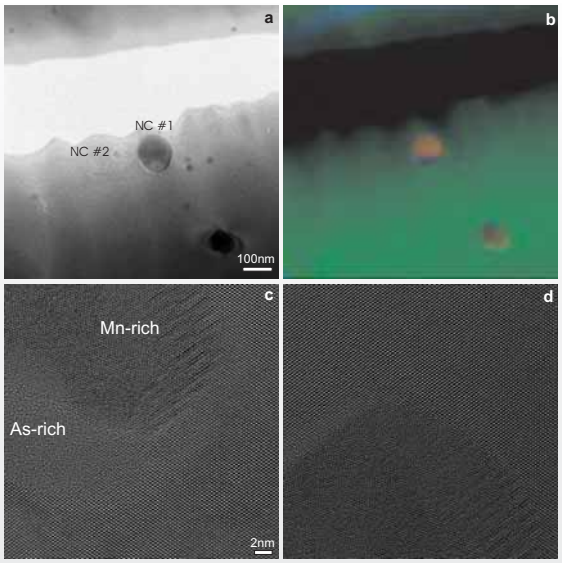

Figure 3. Fig. 3a shows a zero-loss (20eV) EFTEM image of the sample after annealing. Two Nanocrystals are specially marked. A composed map of EFTEM Mn (red), As (blue) and Si (green) images is shown in Fig.3b. NC #1 appearently consists of a separate Mn-rich and an As-rich phase. Fig. 3c shows a HRTEM image (taken at close to zero C_s) of the interface Mn/As of NC #1. The Mn-rich phase of the nanocrystal is crystalline while the As-rich phase is amorphous. In Fig. 3d a HRTEM image of NC #2 is shown. Here the structure indicates a crystalline MnAs-nanocrystal without a separation of phases

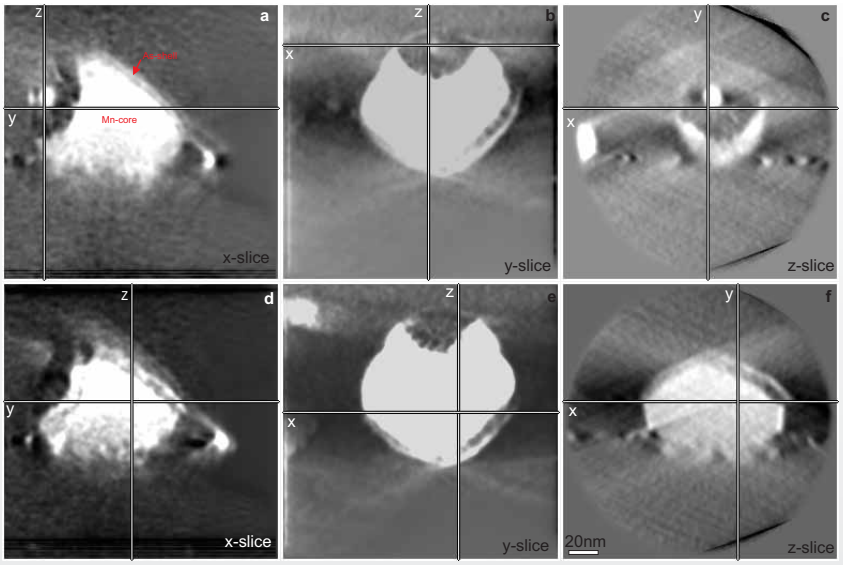

Figure 4. Reconstructed tomogram of the nanocrystal NC #1 shown in Fig. 3a. Fig. 4a,b,c and 4e,d,f are two reconstructions in x,y,z projection and present views from different directions.
The nanocrystal has a core-shell structure that is visible in every slice. Together with the EFTEM-results (Fig. 3b) it can be concluded that a crystalline Mn-rich core is surrounded by a amorphous As-rich shell. Mn [7] and As [8] have different diffusion constants in Si. The higher diffusion rate of Mn leads first to the formation of Mn-clusters in the voids and later then to an enrichment of As around the Mn-rich cluster. Further studies will investigate whether higher annealing temperatures and/or a different ion dose and ratio between Mn and As can change this fact.

Conclusion

The growth of nanocrystals within a crystalline matrix was shown by in-situ TEM. During the annealing process voids within the matrix are growing, leaving space for the foreign atoms. The mobile foreign atoms diffuse into the voids and form the nanocrystals. It was shown by EFTEM and HRTEM that larger nanocrystals consist of a crystalline Mn-rich phase (manganese silicide) and an separate amorphous As-rich phase. The reconstructed 3D structure of these large nanoparticles shows that amorphous As is surrounding a Mn-core and forms a core-shell structure. It can be assumed that the phase separation of Mn and As within the larger nanocrystals depends on different diffusion rates. However, smaller nanocrystals contain both Mn and As in a mixed crystalline phase.

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