NANODIFFUSION AND SEGREGATION IN TECHNOLOGICALLY IMPORTANT SEMICONDUCTORS

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I. Investigation of segregation kinetics and diffusion of Sb in amorphous Si

Auger Electron Spectroscopy (AES) measurements – Computer Simulations

Before starting this project, we had already investigated the amorphous Si/crystalline Sb bilayer system by means of Auger electron spectroscopy. The preliminary results indicated that the a-Si/c-Sb is a phase separating alloy, with strong segregation tendencies and surprisingly high Sb solubility and diffusivity [1]. The solubility and the diffusivity parameters were estimated to be many orders of magnitude higher than the same parameters in crystalline Si. To understand the details of the kinetics we performed further AES kinetics measurements in Marseille using similar samples as in [1] prepared in Debrecen. In these experiments we used a sample several times in order to see if the diffusion-segregation kinetics is reproducible. Before each kinetics experiment we cleaned the surface by ion sputtering. Interestingly, we observed that the successive measurements for kinetics curves did not coincide. On the basis of our computer simulations, we assume that this is strongly related to the low solubility and relatively strong segregation tendency of Sb in a-Si.

We also performed AES experiments in Marseille using completely amorphous bilayer samples. The samples did not contain anymore pure crystalline Sb, but amorphous Si and amorphous $Si_{1-x}Sb_x$ (very probably) oversaturated solid solution layers: a-Si/a-$Si_{0.97}Sb_{0.03}$/substrate. These samples were prepared using magnetron-aided sputtering in Debrecen. However, surprisingly we could not observe any Sb on the surface during heat

treatments. Even at very high temperatures and after very long time. Computer simulations showed that this is probably due to the fact that the system could decrease its free energy faster if the Sb segregates on the a-Si$_{0.97}$Sb$_{0.03}$/substrate interface. That is why the Sb does not escape onto the free surface after diffusing through the a-Si layer.

Secondary Neutral Part Mass Spectrometry (SNMS) measurements – Computer Simulations
As the exact value of the solubility limit of Sb in a-Si had still not been known, moreover, to determine the diffusivity of Sb in a-Si from direct diffusion measurement, we have mapped the profiles by means of SNMS technique. We performed the experiments mainly in trilayer geometry: a-Si/a-Si0.97Sb0.03/a-Si/susbtarte. These samples were also prepared using magnetron-aided sputtering in Debrecen.

Several dozens samples have been measured by SNMS technique before and after heat treatments at 450-600°C. Fitting the composition profiles by continuum diffusion equations, we tried to determine the diffusion coefficients. However, unfortunately the change of the composition profile was not significant enough to deduce the diffusion coefficient accurately. We increased the temperature of the heat treatments to achieve more significant change in the composition profiles but at elevated temperatures (600°C) the samples crystallized as we showed by transition electron microscopy (TEM). It is worth noting here that the crystallization temperature differs significantly from values given in the literature (about 700°C).

It is interesting to note that we could never detect Sb in the a-Si by means of SNMS technique, although some Sb must have been in the a-Si after heat treatment especially at elevated temperatures. The TEM pictures showed that the whole sample, i.e. also the a-Si was crystallized. The temperature during the heat treatments was much lower than the crystallization temperature of the pure a-Si (750 °C). Thus we conclude that the Sb atoms diffused into the a-Si and induced the crystallization (known in the literature as metal induced crystallization). This means that the Sb content was below the detection limit of the SNMS, which is about 0.1 %. This gives an upper limit estimation for the solubility limit of Sb in a-Si.

The clear understanding of the details of the diffusion-segregation kinetics of Sb in a-Si needs doing some further experiments, we presented some

of our results in an international conference (JVC-11, Prague 2006) and the article submitted to this conference will be published in the refereed journal, Vacuum [2].

II. Investigation of the dissolution of Si into amorphous Ge, study the kinetics of interfaces shift by AES

Using AES depth profiling we showed that interfaces in amorphous Si/Ge multilayers remained sharp and shifted during heat treatments [3]. However, the kinetics of the interface shift has not been measured.

For the observation of the interface shift in amorphous systems, we prepared a thin ($\sim$3 nm) Si film on the surface of a thicker ($\sim$100 nm) amorphous Ge layer by magnetron sputtering in Debrecen, and the dissolution of Si was tried to follow by AES in Marseille. However, unfortunately the Si layer contained to much decontaminants also in its volume, thus we could not perform this measurement in this way. For this reason, in Debrecen we prepared only the thick a-Ge layer on a substrate and than we put it in the Auger apparatus in Marseille. In the experimental chamber we sputtered the surface the a-Ge until it was clean. Then we deposited the a-Si on the top of it. In this way me managed to measure some dissolution kinetics and determine the kinetics exponent similarly to that published in [4]. Although the measured points have significant uncertainties, the preliminary results are very promising. They indicate that the kinetics differs from the Fickian one. To confirm these preliminary results, we plan to repeat these measurements under better conditions, namely we would like to prepare also the a-Ge layer in-situ and perform the measurement by X-ray Photonemission Spectroscopy (XPS), which is more sensitive for the Ge than the AES.

References

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