

Concentration dependent pair-correlation in amorphous $\text{Si}_{1-x}\text{Ge}_x$ layers revealed by micro-combinatorial TEM

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Introduction

Our aim was to effectively TEM study the pair-correlation properties ie. average distances of adjacent atoms of a-Si-Ge as a function of Ge concentration in amorphous $\text{Si}_{1-x}\text{Ge}_x$ layers at the entire composition range. We applied micro-combinatory based on the "one-sample concept" in which a gradient sample was prepared and studied in a single TEM grid representing a whole binary system A_xB_{1-x} ($x=0\ldots1$) [i, ii]. Thanks to all-in-one feature of the μ -combinatorial TEM specimen no need for laborous preparation, replacement and study of a series individual samples. Beside effectivity a specific advantage of μ -combinatory is that various compositions are formed and investigated side by side, within a single TEM grid that provides superior reproducibility and direct comparison for EDS and SAED measurements.

Experimental

8 nm thick Si-Ge composition spread samples have been deposited by dual DC magnetron sputtering onto Czochralsky-grown NaCl single crystals in a stainless steel UHV vacuum system of 3×10^{-8} mbar base pressure. The freshly cleaved substrates were mounted inside the micro-combinatorial device that was introduced into the vacuum chamber through an airlock. After evacuation 3×10^{-3} mbar Ar gas was introduced and the gradient SiGe samples were deposited by the two (Si and Ge) power-regulated magnetron sources through a 100 μm wide slot that was sweeping above the substrate. The combinatorial layer track was 1mm wide and 2.5 mm long that fits to the view field of the TEM. The length of the track condensed 3 sections: 0.5 mm of Si, 1.5mm of Si-Ge (gradient section) and 0.5 mm of Ge. The preparation technique of μ -combinatorial samples was described, in detail, earlier [ii]. After removal from the vacuum system the samples were wet-stripped from the NaCl and placed on Cu TEM grids with rectangular mesh so that the gradient line was oriented diagonally to the grid bars. This assured that none of the compositions were masked out by the grid bars.

The composition spread SiGe sample was investigated by a conventional PHILIPS CM20 200kV TEM equipped with a BRUKER SDD EDS system and a 300kV JEOL 3010 HRTEM of 0.17 nm point resolution equipped with a GATAN TRIDIEM EELS.

During TEM measurements a series of selected area electron diffraction (SAED) patterns were recorded with carefully controlled and reproduced camera length and lens currents along the gradient film representing various Si-Ge compositions. The local composition was determined with energy Dispersive Electron Spectrometry (EDS) by a Bruker Si-drift detector system. The intensity distribution of SAED-s were determined with help of the software "ProcessDiffraction" [iii] and the nearest atomic distances in the amorphous Si-Ge were calculated and plotted as a function of the elemental composition.

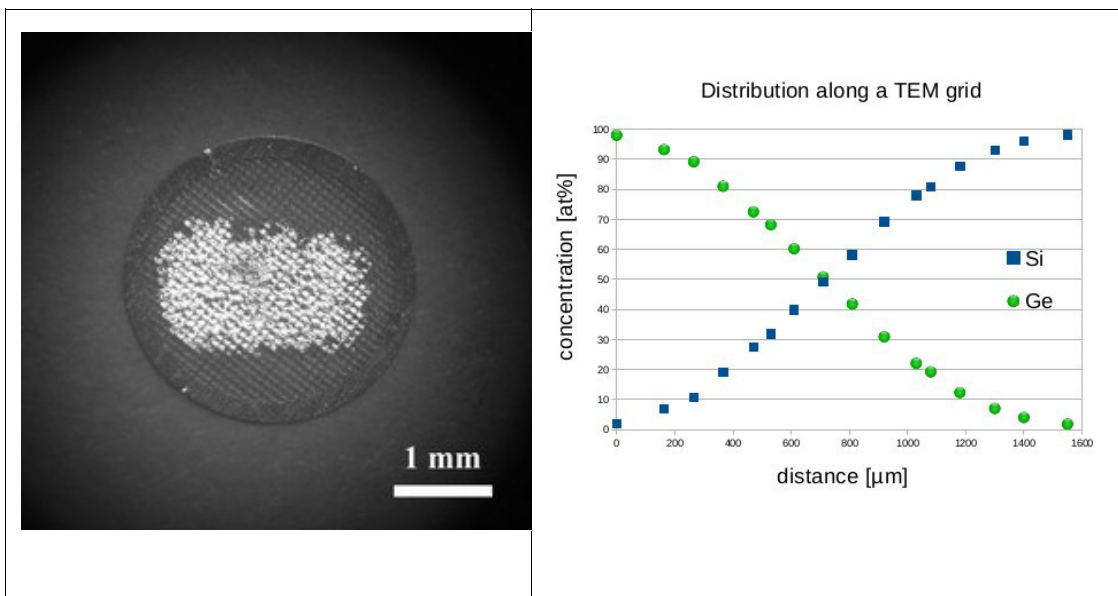


Fig. 1. (a) Overview of an ultrathin (8 nm) concentration-spread μ -combinatorial SiGe sample deposited on Mo TEM grid. The $1 \times 2 \text{ mm}^2$ sized layer consists of a $1000 \text{ }\mu\text{m}$ long concentration gradient Si-Ge track enclosed by $250 \text{ }\mu\text{m}$ long tracks of pure Si and Ge. (b) Concentration distribution revealed by EDS along a horizontal scan of the μ -combinatorial TEM specimen shown in (a).

Figure 1 (a) shows the overview of the $1 \times 2 \text{ mm}^2$ size combinatorial Si-Ge sample. It consists of three sections: a $1000 \text{ }\mu\text{m}$ long stripe with a concentration gradient enclosed by $250 \text{ }\mu\text{m}$ long stripes of pure Si and Ge. The Si-Ge concentration distribution as a function of distance along the TEM grid plotted in Fig.1 (b) was measured by EDS in the TEM. The diagram shows an acceptably linear concentration variation with a gradient of $0.1 \text{ at\%} / \mu\text{m}$, except at the transition from single to binary component regions.

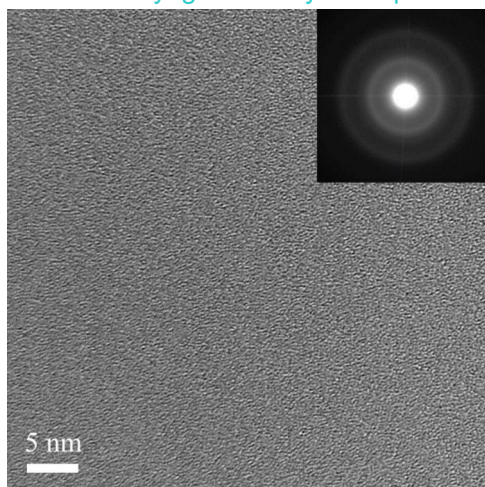


Figure 2. TEM micrograph with SAED inset of the ultrathin 8 nm self-supporting micro-combinatorial amorphous SiGe sample at 50/50 at% composition.

Fig. 2. shows a bright field TEM with a SAED inset at 50/50 at% SiGe composition of the concentration spread sample. Both TEM and SAED represent amorphous structure, that was found at all compositions of the sample.

Atomic distances of a-Si-Ge as a dependence of Ge concentration

Both crystalline Si and Ge form fcc diamond structure with lattice parameters, Si: 0.357 nm [iv], Ge: 0.357 nm [v]. Applying Vegard's rule ($a(\text{Si}_{1-x}\text{Ge}_x) = (1-x) a(\text{Si}) + x a(\text{Ge})$) we calculated the atomic distances (a) of the nearest neighbours in a-Si-Ge as a dependence of Ge concentration. These theoretical atomic distances are represented by the solid line in fig. 3. Deviations from adjacent atomic distances, determined from SAED measurements of the sample of varying composition, from Si are indicated in the same diagram by squares. It is clearly seen, that the squares at the ends of the gradient range (pure Si and pure Ge) show very good fit to the calculated Vegard line, while in the gradient range (mixed compositions) they typically fall above the Vegard line. The measured values, therefore, are “forward” compared to what is calculated - that is, they show an atomic distance corresponding to a higher Ge concentration.

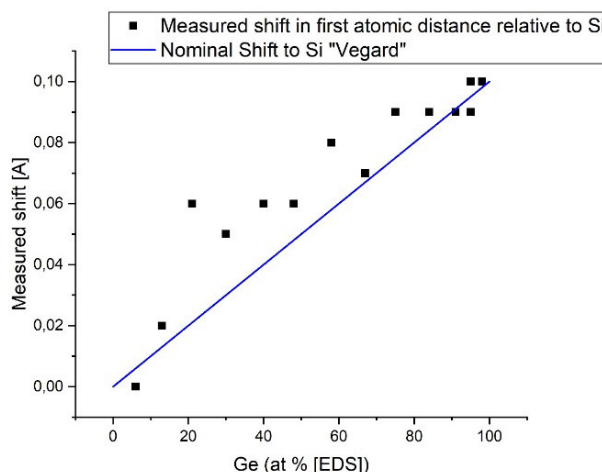


Figure 3. Deviations of adjacent atomic distances from that of Si in an 8 nm thick μ -combinatorial a-SiGe sample, as a function of Ge concentration: determined from SAED measurements (square) and calculated according to the Vegard's rule (solid line).

To explain the difference between the Vegard line and the experimental result, we need to consider the different oxygen affinities and behaviour of the two elements: In the thermal oxidation of amorphous SiGe mixed layers, it was found that exclusively SiO_2 is formed on the surface at first, which is accompanied by Si transport and enrichment of Ge under the surface oxide layer. The oxidation of Ge takes place only after the oxidation of the total amount of Si [vi]. It is to note that the selective oxidation mechanism also has technological importance; proposed to form an ultra-thin Ge-rich SiGe layer in CMOS-SOI technology [vii, viii, ix]. In the present study, we concluded that, similarly to the above, selective oxidation of Si took place in the combinatorial SiGe thin film under normal environmental conditions. Due to Si bound in SiO_2 , the elementary Si / Ge ratio shifted in the Ge-rich direction, obviously, this caused the deviation of the result measured by SAED from the Vegard rule (Figure 3). It is to note that the layer showed an oxygen content of up to 20% as measured in TEM by EDS. It is easy to see that in an ultra-thin sample of 8 nm in thickness a few atomic layers (~ 1 nm) of native SiO_2 , preferably formed on the two free surfaces may bind a significant proportion of Si, hence changing the elemental Si / Ge ratio in the Ge-rich direction.

Conclusion

The average adjacent atomic distances were revealed in the entire composition range as a function of Si-Ge composition. They follow the Vegard's rule in the trend, but due to selective oxidation of Si, the diagram advances towards the values characteristic of Ge-rich compositions.

Acknowledgements

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