

S. Oswald · S. Baunack · G. Henninger · D. Hofman

## Model investigations on the effect of Si transport on the nanocrystallization of amorphous FeSiB-(Cu,Nb)

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**Abstract** Amorphous material of the class FeSiB-(Cu,Nb) has been investigated with a background of soft-magnetic application of the corresponding nanocrystalline material. Thin-film analytical methods (SIMS, AES, TEM) have been used to study the diffusion of Si in such materials prepared as layer systems by magnetron sputter deposition. Significant interdiffusion occurs even at low temperatures – approximately 400°C. Quantitative description failed, however, because formation of new iron monosilicide phases begins above this temperature. It is concluded that only high-mass-resolution SIMS or radioactive tracer analysis can be used for successful acquisition of information at this material system.

**Keywords** Diffusion · Nanocrystals · Phase formation · Magnetic material · Depth profiling

### Introduction

In the development of modern soft-magnetic applications there is much interest in nanocrystalline materials. One class of such material is FeSiB-(Cu,Nb) alloys [1, 2] which can be prepared as tapes by rapid quenching or as thin films by physical vapor deposition (PVD) [3]. The specific soft-magnetic properties are obtained by deliberate crystallization from the initially amorphous state by use of well-defined thermal treatment. The microstructure obtained in this way consists of Fe<sub>3</sub>Si nanocrystals, with

diameters in the range 10–20 nm, embedded in a residual amorphous matrix. Before the crystallization Cu is believed to form clusters [4] whereas Nb is believed to hinder crystal growth during the crystallization, maintaining and stabilizing the nanocrystalline grain structure [1]. During the crystallization the redistribution of Si is considered an important factor.

This report describes a study of diffusion and phase formation in FeBNb(Cu)/Si/FeBNb(Cu) thin-layer systems by means of thin-film characterization methods such as secondary-ion mass spectrometry (SIMS), Auger electron spectroscopy (AES), and transmission electron microscopy (TEM). The main idea was to simulate the residual amorphous phase which remains when the Fe<sub>3</sub>Si nanocrystals are formed with the FeBNb(Cu) layer, and thus to model Si transport in this phase [5, 6].

SIMS is a depth-profiling method for trace element analysis with typical detection limits in the ppm range. It is, therefore, alongside methods which use radioactive tracer material, a standard method for investigation of diffusion processes [7, 8]. The main problem of SIMS analysis is, however, quantification, because ionization probabilities vary by orders of magnitude, depending on the chemistry of the surface – this is the so called “matrix effect”. To minimize this effect quantitative SIMS depth profiling usually uses reactive primary ions; in our work we use oxygen, which leads to oxidation of the outermost surface and to stable measurement conditions for positively charged secondary ions [9].

The classical diffusion experiment uses the “thin source” model (“delta” distribution of the diffusive element located between unlimited regions of the matrix), because mathematical description is very easy [10] and phase formation with the matrix can be neglected, because of the low content of the diffusive element [7]. Matrix effect in SIMS plays also no role, because of the high dilution. We wished to model this with “thin Si interlayer” samples.

The other possibility is the “unlimited source” method, in which unlimited regions of the matrix and the diffusive element are assumed to be connected by one interface

S. Oswald (✉) · S. Baunack · G. Henninger · D. Hofman  
Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden,  
Postfach 270016, 01171 Dresden, Germany  
e-mail: s.oswald@ifw-dresden.de

#### Current addresses:

G. Henninger,  
Philips GmbH, Philipsstr.8, 52068 Aachen, Germany

D. Hofman,  
Infineon Technologies AG,  
P.O. Box 80 09 49, 81609 München, Germany

area [10]. Here mathematical description is again relatively easy, although interdiffusion of the matrix elements must be considered, and, because of the high concentrations involved, formation of new phases can also occur. These changes in the main concentrations can also lead to artifacts, because of the SIMS matrix effect. This situation was approximated by use of the “thick Si interlayer”.

In diffusion studies AES depth profiling can be used to investigate changes in the concentrations of the main elements, down to the typical detection limit of this method of approximately 0.1 %. If formation of compounds or phases occurs the shape of the Auger peaks of any element can change, because of variations in binding energy, the shape of the valence band, relaxation effects, or intrinsic or extrinsic losses [11]. For detection and separation of changing peak shapes factor analysis of the recorded set of spectra is nowadays routinely used [12, 13].

## Experimental

### Sample preparation

The multilayer samples were prepared by DC-magnetron sputtering on to oxidized silicon wafers by using the typical deposition parameters: power 50 W and argon pressure  $5 \times 10^{-3}$  mbar. The targets were an alloy  $\text{Fe}_{51.2}\text{B}_{31.1}\text{Nb}_{13.3}\text{Cu}_{4.4}$  (and a similar alloy without Cu) and pure Si.

Two kinds of sample were prepared. For the thin Si interlayer the intended structure was FeNbCu (40 nm)/Si (2 nm)/FeNbCu (42 nm), resulting in a total thickness of approximately 85 nm. For the thick Si interlayer the layer stack was FeNbCu (80 nm)/Si (65 nm)/FeNbCu (85 nm) and the total thickness was 230 nm. The measured total film thicknesses were found to be in good agreement with the results from TEM cross-sections (Results section). Thermal annealing was performed in a tubular furnace under vacuum at 400, 475, and 550 °C for 1, 4, and 16 h, respectively.

### Depth profiling

The SIMS experiments were performed out with an IMMA micro-analyzer (ARL) using  $\text{O}_2^+$  primary ions at 8.5 or 18.5 keV under normal incidence of the primary ions, an ion current of approximately 40 nA, and a raster size of  $300 \mu\text{m} \times 300 \mu\text{m}$  (measurement

area  $100 \mu\text{m} \times 100 \mu\text{m}$ ). Positively charged secondary ions were analyzed in a magnetic mass analyzer with low mass-resolution.

For AES depth profiling we used a PHI 660 microprobe (Physical Electronics) with primary electrons of 10 keV impinging at  $30^\circ$  to the surface normal. The samples were sputtered with 1.5 keV argon ions at  $60^\circ$  to the normal. The corresponding etch rate in  $\text{SiO}_2$  was approximately  $3 \text{ nm min}^{-1}$ . Factor analysis of the spectra recorded during depth profiling was performed with user-written MATLAB routines.

### Transmission electron microscopy

TEM measurements were performed to study phase formation more quantitatively. The TEM cross section specimens were prepared by the conventional face-to-face technique with sticking, grinding, and ion milling. Measurements were performed with a Philips microscope CM20 FEG equipped with a Gatan PEEL 666 spectrometer for electron energy-loss spectrometry (EELS).

## Results

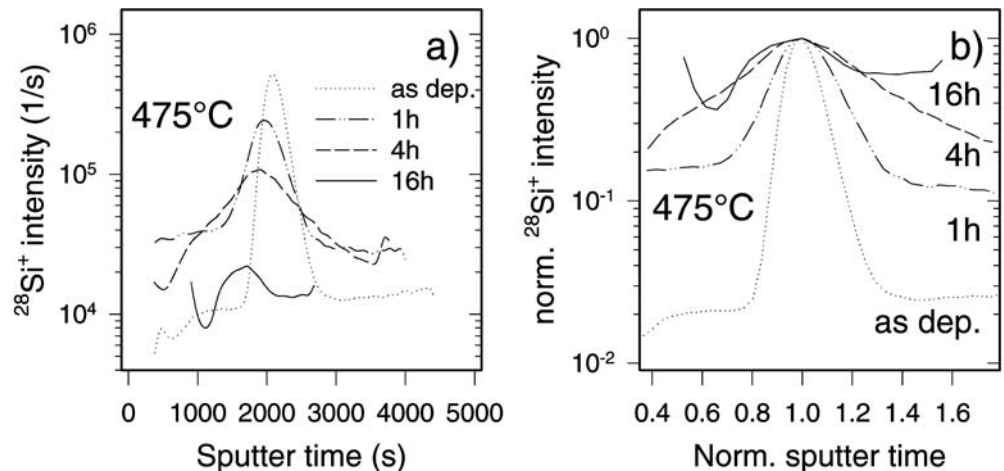
### SIMS depth profiles

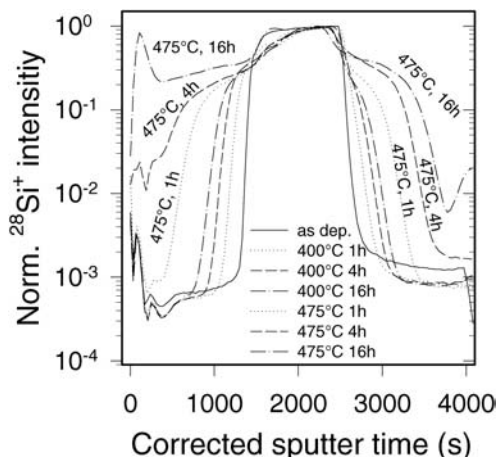
Measurements on the “thin Si interlayer” showed that at 400 °C no significant diffusion effect could be observed. The measurement results at 475 °C are shown in Fig. 1a. Because of differences between the sputtering conditions (ion current fluctuations) in the several experiments, for purposes of comparison the profiles were also normalized to their maximum intensities on both the intensity scale and the sputtering time scale (Fig. 1b).

Although significant diffusion was observed, quantitative description was not possible because the dynamic range of the data emerging from a relatively high measuring background (Fig. 1b) produced by  $\text{Fe}^{2+}$  clusters was too low. Results obtained at 550 °C were quite similar to those at 475 °C – even after treatment for 1 h very strong diffusion was observed.

For this reason we had to concentrate on the results from the “thick Si interlayer” sample series. In Fig. 2 the silicon depth profiles are shown for the as-deposited state and for the samples annealed at 400 and 475 °C. The pro-

**Fig. 1** SIMS depth profiles for silicon in the thin Si interlayer sample in the as-deposited state and after annealing at 475 °C: (a) measured  $^{28}\text{Si}^+$  intensity; (b) normalized  $^{28}\text{Si}^+$  intensity profiles.

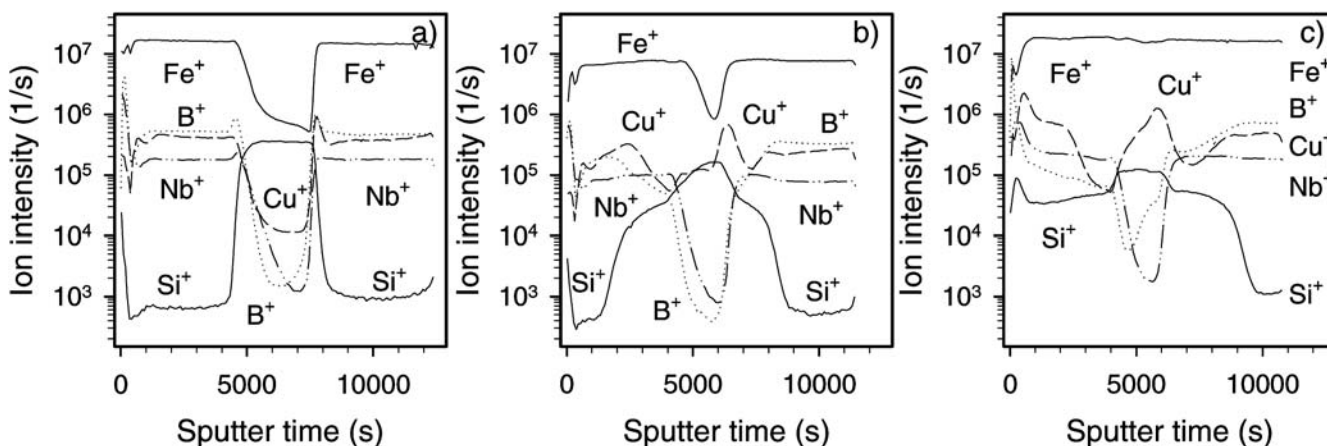




**Fig. 2** SIMS depth profiles for the thick Si interlayer sample. The normalized  $^{28}\text{Si}^+$  intensities are shown for the as-deposited state and after annealing for different times at 400°C and 475°C.

files were normalized to their maximum intensity and the time scale was corrected by use of the Nb depth profiles. As will be apparent later from Fig. 3 (and also from discussion of the AES results) the Nb profile is the only profile that does not change significantly; it can, therefore, be used for depth-scale correction. From Fig. 2 it is obvious that even at 400°C significant transport of Si occurs. This seems to contradict the above observation of no diffusion at that temperature for the thin source and is probably caused by a preferential diffusion from material of the FeNbB layer into the Si layer, which changes, in parallel, the matrix composition and diffusion behavior in this interface region. Study of the changes in the shape of all elemental depth profiles at the interfaces between the layers (see also Fig. 3) suggests that Fe (and the minor element Cu) can be assumed as to be a candidate for such diffusion (see also discussion of TEM results, below). In general surface enrichment (oxidation) is observed and the non-

**Fig. 3** SIMS depth profiles of the main constituents of the thick Si interlayer sample in the as-deposited state (a), and after annealing at 475°C for 1 h (b), and for 16 h (c).



symmetric shapes of the profiles are indicative of regions with different diffusion coefficients, or of phase formation at the interface regions. For comparison the SIMS depth profiles of the main constituents in the as-deposited state and after annealing at 475°C for 1 h and 16 h are shown in Fig. 3. These results are indicative of substantial interdiffusion of all elements except Nb.

Diffusion coefficients can be determined from SIMS profiles only if the intensities are proportional to the concentration, i.e. it must be proven that no new phases are formed.

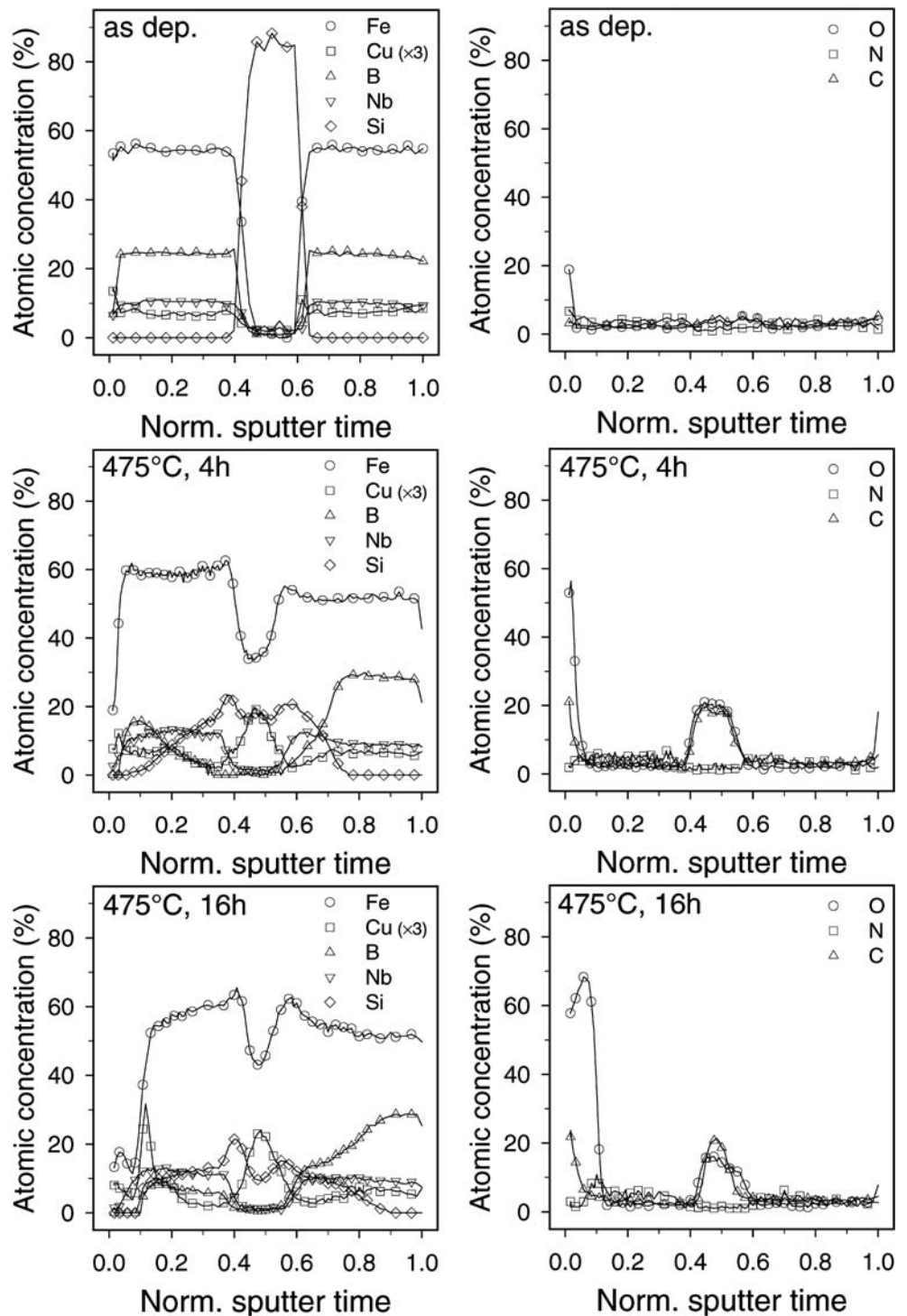
#### AES depth profiles

AES depth profiling of the thin-film sample suffered from the low dynamic range in the same way as SIMS. The depth profiles for the main constituents of the thick film sample in the 475°C series after 4 and 16 h are given in Fig. 4, in which they are compared with the as-deposited state. For greater clarity the profiles of the main elements are plotted on the left of the figure and the profiles of the impurities are plotted on the right. The results show that, as already supposed from the SIMS measurements, during annealing complete intermixing of most elements occurs. In addition, characteristic peak shapes change; results from a factor analysis procedure are indicative of formation of a phase including the elements Fe and Si (Fig. 5).

The following main features can be summarized from the AES depth profile results.

1. As already mentioned for the SIMS results Nb is the only element not participating in the interdiffusion – the profiles are not changed (Fig. 4, left).
2. B diffuses outwards to the surface; the outermost FeNbB layer lost most of the B (Fig. 4, left).
3. Cu becomes segregated in the Si interlayer (4 h, 16 h) and also moves to the sample surface (16 h) (Fig. 4, left).
4. From the factor analysis results for the Si peak (Fig. 5) it can be assumed that interdiffusion of Fe and Si leads to a new phase (or new phases), at first at the interfaces (1 h, 4 h) and then also in the complete Si interlayer (16 h).

**Fig. 4** AES depth profiles for the thick Si interlayer sample annealed at 475 °C for different times: *left column*, concentrations of the main constituents; *right column*, concentrations of the impurities. The data are given as the lines; the symbols are to guide the eye.

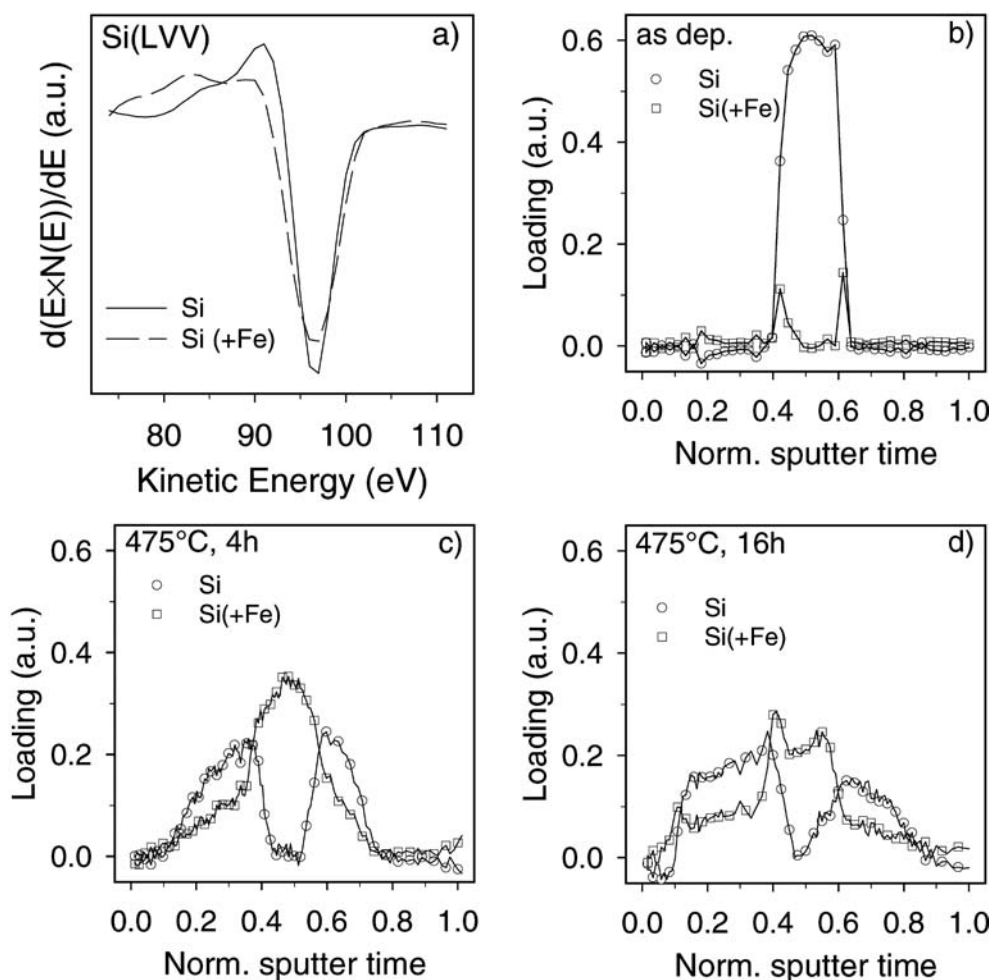


5. In addition to approximately 4 atom% N in the FeBNbCu layer from the preparation, enrichment of carbon and oxygen occurs in the Si interlayer during thermal treatment (4 h, 16 h; Fig. 4, right). After 16 h severe surface oxidation also occurs. This is assumed to be caused by residuals in the atmosphere during annealing.

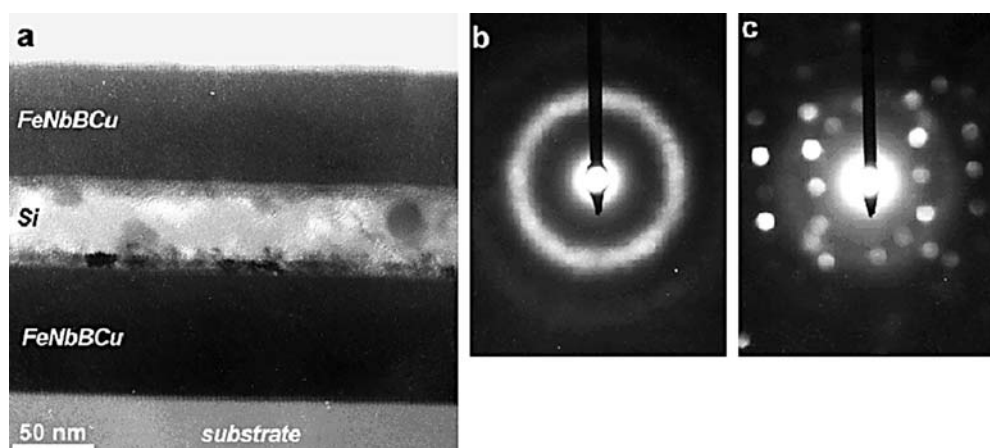
TEM investigations

In the as-deposited state all the layers are completely amorphous. The nominal thicknesses from the preparation could be confirmed. In the “thick film samples” typical roughness of the interfaces of approximately 3 nm was found. As could be assumed from the preparation conditions in the “thin film sample”, the Si interlayer can be detected only as a very small contrast change in a region of

**Fig. 5** Results from factor analysis of the Si(LVV) transition for the thick Si interlayer sample. Two characteristic peak shapes (a) are found which are assumed to be pure Si and Si with Fe. Depth profiles of the loadings of these two components in the as-deposited state (b), and after annealing at 475 °C for 4 h (c) and for 16 h (d).



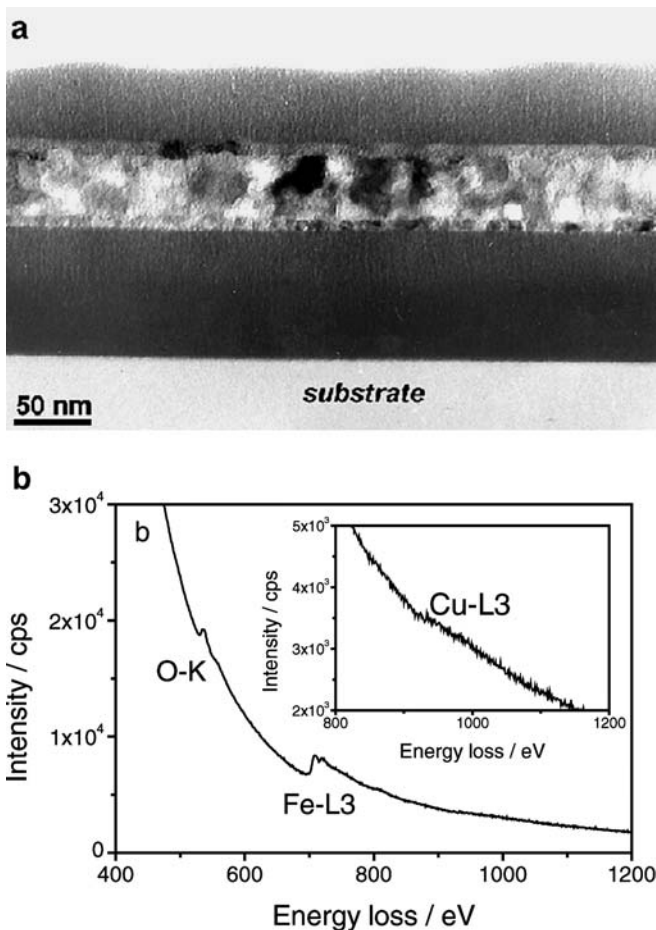
**Fig. 6** Thick Si interlayer sample after annealing at 475 °C for 1 h: (a) TEM cross-section micrograph, and electron diffraction pattern of (b) the amorphous FeBNbCu layer and (c) the interface layer within silicon (FeSi, zone axis [1 1 0]).



2 nm, which also should be the region of the roughness from the preparation process.

The structure of the layer system is completely changing during annealing. After annealing at 475 °C for 1 h crystalline interlayers approximately 10 nm thick are created at both interfaces of FeBNb with Si (Fig. 6a). By means of EELS Si and Fe could be detected there at the side of the original silicon layer. That means that Fe has diffused into the silicon, which is in agreement with ex-

pectations from the SIMS results. Microdiffraction patterns (Fig. 6c) could be best approximated in simulation calculations with FeSi (cubic, lattice constant 0.449 nm, structure type B20, space group P2<sub>1</sub>3) as a possibly newly formed phase; the small crystallite sizes, however, complicate their identification and other silicide phases cannot be completely excluded. Most of the FeBNb(Cu) layer remains in the amorphous state (Fig. 6b). After annealing for 4 h an increasing number of growing crystallites (up



**Fig. 7** Thick Si interlayer sample after annealing at 475°C for 4 h: (a) TEM cross-section micrograph, and (b) electron-energy-loss spectra of the crystalline interlayer for detection of oxygen, iron, and copper (beside silicon – not shown).

to 40 nm size) could be seen in the Si interlayer also (Fig. 7a). By use of EELS beside Si, Fe, and O, Cu also was found in the Si interlayer (Fig. 7b). Unambiguous identification of the microdiffraction patterns is not simple, because the crystallographic similarity of the phases had to be taken into consideration. Possible phases are iron silicides (FeSi or FeSi<sub>2</sub>) or iron oxide (Fe<sub>3</sub>O<sub>4</sub>).

All these TEM results are in good agreement with the AES results discussed above and confirm the drastic changes in the samples during annealing.

## Conclusions

From these investigations it can be concluded that in the material studied Si transport is overlaid by phase formation even at relatively low temperatures. Iron monosilicide is assumed to be formed as the first stable Fe-Si phase. It is, therefore, not possible to determine diffusion coefficients for diffusion of Si in the FeBNb(Cu) amorphous layers quantitatively using a thick Si interlayer as the source for diffusion. We also observed outward diffusion of B to the sample surface and an influence of O and C residuals from the annealing atmosphere. This should be prevented by use of a capping layer (e.g. a stable nitride) on top of the layer system. Because of the phase formation it is only suitable to use the “thin Si interlayer” in connection with SIMS in high-mass-resolution mode (to separate Si<sup>+</sup> and FeX<sup>2+</sup> ion species) or using an isotope technique with nuclear markers. Diffusion in the real amorphous FeSiBNb(Cu) material could also be investigated by use of the latter technique.

This behavior is, in principle, similar to that observed during investigations on a copper-free FeBNb model layer system.

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