Interface sharpening in miscible Ni/Cu multilayers studied by atom probe tomography

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Interfaces of Ni/Cu multilayers were studied by atom probe tomography. To this aim, specimens with sharp or artificially smeared interfaces were prepared and investigated before and after annealing at 773 K. Owing to three-dimensional subnanometer resolution of the atom probe, local chemical analysis of layer interfaces becomes possible without interferences of grain boundaries or geometric roughness. In contrast to the classical expectation for a miscible system, but in agreement with more recent theoretical considerations, diffusion reduces the chemical width of the interfaces by up to 50%. © *2011 American Institute of Physics*. [doi:10.1063/1.3658390]

With decreasing characteristic length, density, and relevance of interfaces, such as phase or grain boundaries (GB), increase and may control the physical properties of nanostructured materials.[1] The abruptness of the interface between different phases can be crucial for various technologies from soft X-ray mirrors[2] to hard disk reading heads.[3] Real interfaces can never achieve perfect chemical sharpness both because of practical reasons (e.g., ballistic mixing or dynamical segregation during production) and thermodynamic mechanisms (gradient energy terms in the thermodynamics of inhomogeneous systems warrant a limited sharpness in the case of immiscible systems[4,5]). On the other hand, if mixing energy is zero or negative and both components are miscible, the equilibrium "interface" becomes infinitely broad. But the time to reach this equilibrium is long, and in intermediate states the chemical structure of the interface may be controlled by kinetic constraints. Recently, it was pointed out that chemical mixing by diffusion may even lead to sharpening of interfaces, if atomic mobilities in both phases differ by some orders of magnitude.[6] The explanation is straightforward. If the diffusivity decreases strongly with increasing A-atom concentration, movement of atoms in the pure A-phase and in the A-rich part of the interface is difficult. Consequently, intermixing is negligible there. Diffusion in the B-rich part of the interface is active however; accordingly it can reach equilibrium with the pure B-layer by redistributing homogenously all available A-atoms. This leads to a situation, where a B-phase with randomly distributed A impurity atoms is separated from a pure A phase by a sharp interface. Although confirming the effect in theoretical Monte-Carlo simulations, a more recent study raises doubts whether the effect can really take place in rough or already partly intermixed interfaces.[7]

Measuring the width of interfaces accurately is challenging, as a variety of phenomena may appear as increased diffuseness. Misaligned, curved or rough interfaces cause artifacts. So the practical resolution will be much lower than the instrumental limits of a certain method. Techniques providing an average over a larger volume or surface area (e.g., X-ray[6] or neutron beam based methods, Auger analysis) include signals of GBs and other defects, which may produce artifacts in data evaluation or interpretation. An ideal method to study interfaces must therefore be local, projection-free, and chemically sensitive in subnanometer range.

While not without its own challenges, atom probe tomography (APT) comes close to these criteria. APT is based on controlled field desorption. Atoms are removed one-by-one from a tip-shaped specimen, and their detector position and flight time are recorded. From these data, chemical identity and original position of the incoming particle are determined by numerical evaluation. As a result, a full 3D chemical reconstruction of the sample is possible with subnanometer resolution (see Fig. 1). Local profiling can be carried out in any arbitrary direction and position of the sample. In analyzing an interface, a spot far away from disturbing diffusion fields of structural defects can be selected. Current wide angle instruments with high frequency HV- or laser-pulsers are capable of analyzing a volume of $100 \times 100 \times 1000$ nm^3 within a timescale of a few hours or days at maximum.[8,9] Accordingly, a statistically significant number of interfaces can be studied by an adequately fast method. Accurate analysis of multilayer interfaces with APT is nowadays well established[5] even with isotope multilayers.[10,11]

The goal of this work is to verify the kinetic interface sharpening[6,7] by a truly atomistic method, by which the interface diffuseness can be clearly separated from any other phenomena. We chose the Ni/Cu system since it is miscible at the 773 K annealing temperature, well known to have an asymmetry in partial mobilities, and representing one of the earliest demonstrations of a Kirkendall-shift[12] and a non-Fickian dissolution kinetics,[13] too. Ni/Cu multilayers also attracted interest due to beneficial magnetic properties and ease of preparation in ultrafine thickness.[14,15]

We prepared Ni/Cu multilayers on flat W-post by a purpose built UHV ion sputtering device following the procedure of Ref. 16. We blunted electropolished W-tips by FIB

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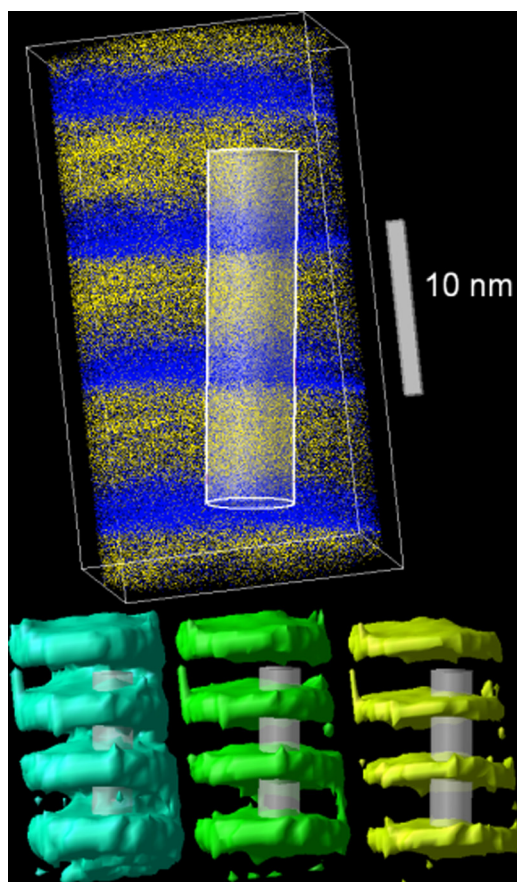
FIG. 1. (Color online) Tomographic reconstruction with analysis cylinder. Ni and Cu atoms are represented by blue (darker) and yellow (brighter) pixels, respectively. The scale bar on the left is 10 nm long. To compensate local roughness or misalignment, the analysis cylinder has to be tilted. Below, from left to right are the 30at%, 50at%, and 70at% isoconcentration surfaces used to determine the local composition gradient.
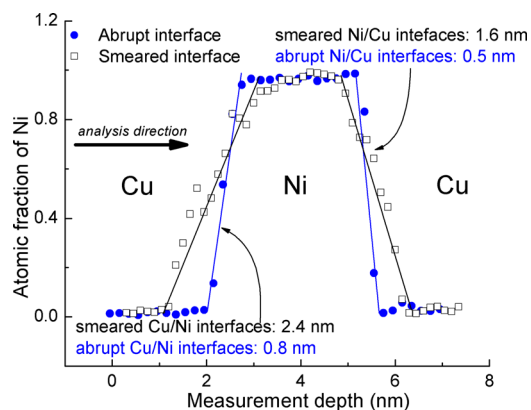

FIG. 2. (Color online) Comparison of a Ni layer with (black, open symbol) and without (blue, full symbol) artificially smearing of the interface. By wiggling the sputter targets, the interface width has been increased from 0.8-1.0 nm to 2–4 nm in case of Cu/Ni interface (right) and from 0.4–0.6 nm to 1-2 nm in case of Ni/Cu interface (left).

to achieve a smooth, flat, circular surface of 1-2 μm radius. This acts as a substrate for a $(Ni_{4nm}Cu_{4nm})_{20}$ multilayer stack. A thicker Cu spacer was placed between the W and the stack as well as a protective Cu cap on the top. The specimens show a slight variation in thickness depending on their position in the sample holder. Some specimens were heat-treated at 773 K for 15 min while others were left in as-prepared state. After preparation and annealing, the samples were FIB-milled to achieve a conical shape with a hemispherical cap of less than 50 nm radius. The finished samples were investigated using the atom probe instrument at University of Münster.[17]

The distinguishing feature of this study is that the chemical transition at the interface was artificially smeared for some specimens by wiggling between the Cu and Ni targets. Several submonolayers of Ni and Cu atoms were deposited, creating a diffuse interface with an almost linear profile in the as-prepared state. The thickness of the Cu/Ni and Ni/Cu (first stated metal is deposited on top of the second) smeared interfaces was 2-4 nm and 1-2 nm, respectively. For comparison, Cu/Ni and Ni/Cu interfaces were 0.8-1.0 nm and 0.4-0.6 nm thick in samples prepared with abrupt interfaces (see an example in Fig. 2). The significant asymmetry between the two stacking orders is, most likely, a result of the sputtering process (preferred resputtering of Cu while switching to Ni), as it vanished with annealing. This observation also

eliminates the possibility of an instrumental artifact owing to different evaporation properties.

Composition profiles perpendicular to isoconcentration surfaces (see Fig. 1) were determined in both as prepared and annealed samples. In case of the annealed specimens, special care was given to conduct analysis far away from perturbations of diffusion shortcuts (such as GBs, triple junctions, and dislocation bundles). Table I gives a summary of the experimental results. Samples 1ap-3ap, deposited with artificially smeared interfaces in different production cycles, were measured in as-prepared state. Samples 1an-3an, produced together with the respective as-prepared specimens, were analyzed after annealing. Samples 4ap and 4an are control samples produced without target wiggling. Ni and Cu layer thicknesses were determined at 50at% composition levels. To determine interface widths, a straight line was fitted to the concentration profile in the middle of the interface (typically a $\pm$ 25% window around 50at% was chosen). Values stated in the table represent the reciprocal of the slope. We also tested alternative possibilities of profile fitting, as for example spline-fitting[11] or error functions. Because of the difficulty in separating the Cu(Ni) alloy from the interface (see composition profile of the annealed sample in Fig. 3) these methods, however, offered no real benefits compared to the chosen simple straightforward technique. Numerical values of a single sample might be misleading since the destructive nature of APT does not allow measuring the same specimen before and after annealing. Deviations from sample to sample might appear as a result of uncertainties in sputtering process and evaluation. However, the tendency of the complete data set, comprising information of more than 60 individual interfaces, gives us a self-consistent and clear view of the underlying process.

Fig. 3 shows a direct comparison between Sample 1ap and Sample 1an (sputtered together). From the graph, a series of conclusions on the evolution of the system can be drawn. First of all, the difference in width of the Cu/Ni and Ni/Cu interfaces practically vanished by annealing. The remaining difference is within the tolerance limit of measurement. This suggests that the asymmetry in the as-prepared state is not a result of a local magnification effect,[18] but reflects the real state of the specimen; most likely a result

TABLE I. Quantitative analysis of different interfaces. Error marks represent statistical scattering between different interfaces of the sample. Instrumental accuracy, proven in interfacial studies of the immiscible Cu/Ag system (see Ref. 5), is in the 0.3–0.5 nm range.

Sample	Annealing	Ni thickness	Cu thickness	Ni/Cu interf. width	Cu/Ni interf. width
1ap	No	4.0 ± 0.5 nm	4.0 ± 0.5 nm	2.6 ± 0.5 nm	1.4 ± 0.2 nm
2ap	No	4.4 ± 0.5 nm	3.5 ± 0.5 nm	3.0 ± 0.5 nm	1.1 ± 0.2 nm
3ap	No	6.0 ± 0.5 nm	4.2 ± 0.3 nm	3.7 ± 1.0 nm	1.7 ± 0.3 nm
Average of 1ap-3ap				3.1 nm	1.4 nm
1an	773 K 15 min	2.8 ± 0.5 nm	5.2 ± 0.5 nm	1.7 ± 0.3 nm	1.4 ± 0.3 nm
2an	773 K 15 min	3.2 ± 0.3 nm	3.6 ± 0.2 nm	1.5 ± 0.3 nm	1.1 ± 0.2 nm
3an	773 K 15 min	5.5 ± 0.5 nm	5.7 ± 0.7 nm	2.3 ± 0.3 nm	2.1 ± 0.3 nm
Average of 1an-3an				1.8 nm	1.5 nm
4ap	no, non-smeared	2.9 ± 0.2 nm	2.5 ± 0.2 nm	0.9 ± 0.2 nm	0.6 ± 0.2 nm
4an	773 K 15 min, non-sm	2.4 ± 0.3 nm	3.1 ± 0.2 nm	1.7 ± 0.2 nm	1.4 ± 0.2 nm

of the differences in the sputtering/resputtering characteristics of the materials. The symmetrization of the interface widths demonstrates a change from a sputter/production controlled interface to a diffusion-controlled kinetic interface.

Three distinct regions can be observed in the annealed profiles: First, a pure Ni region, which remains largely unaffected by diffusion. However, its thickness significantly shrank in comparison to the as-prepared state. Second, a Cu layer which accumulated a considerable amount of Ni (in the range of 20%). This alloy has grown in thickness when compared to the original Cu layer. The distribution of Ni within these layers is random/homogenous, in agreement with expectations.[13,16] Third, the interfaces became not only symmetrical, but in the particular case of the Cu/Ni interfaces, they sharpened significantly. The initially thinner Ni/Cu interfaces show no significant change but at least they did not broaden opposed to the naïve expectation of a diffusion processes. Consequently, APT confirms clearly the theoretical[7] predictions by direct local, 3D chemical analysis. Comparing the annealed samples of different initial interfaces (Samples 1an-3an to 4an), they show no significant difference. This indicates that the initial width does not play a decisive role in controlling the width of the kinetic interface.
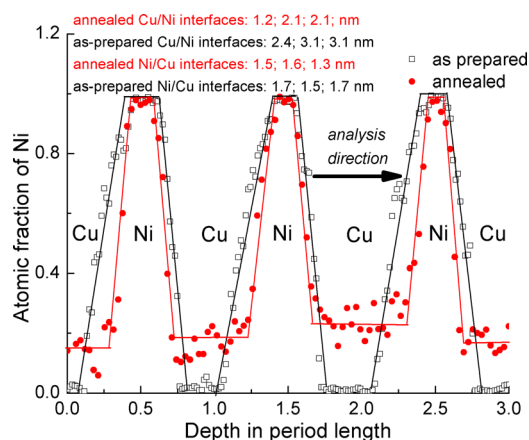

FIG. 3. (Color online) Ni concentration profile of an as-prepared (black, open symbol) and an annealed specimen (red, full symbol). Depth scale is normalized to the respective period length. As a consequence of the mobility difference, Ni layers shrink but remain free of Cu. Cu layers grow but absorb a large amount of Ni; the distribution of Ni in the Cu layer is close to homogenous. Kinetic interfaces, formed after short diffusion, are symmetrical in thickness with respect to layer stacking, although the as-prepared interfaces had shown almost a factor of 2 difference in thickness. A strong sharpening is observed for the Cu/Ni interface. Solid lines represent model-free guide lines.

In summary, we conclude that APT is of great advantage in studying realistic curved, rough or simply misaligned interfaces. Experiments carried out in Ni/Cu multilayers with artificially smeared interfaces definitely confirm that even though thermodynamic equilibrium predicts infinite mixing at the interface, the actual kinetic process, determined by material transport properties, can require nevertheless a finite sharpness in intermediate stages. If the original interface is broader than this kinetic limit, interface sharpening happens.

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