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Investigation of interface properties of Ni/Cu multilayers by high kinetic energy photoelectron spectroscopy

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High kinetic-energy photoelectron spectroscopy (HIKE) or hard x-ray photoelectron spectroscopy has been used to investigate the alloying of Ni/Cu (100) multilayers. Relative intensities of the corelevels and their chemical shifts derived from binding energy changes are shown to give precise information on physicochemical properties and quality of the buried layers. Interface roughening, including kinetic properties such as the rate of alloying, and temperature effects on the processes can be analyzed quantitatively. Using HIKE, we have been able to precisely follow the deterioration of the multilayer structure at the atomic scale and observe the diffusion of the capping layer into the multilayer structure which in turn is found to lead to a segregation in the ternary system. This is of great importance for future research on multilayered systems of this kind. Our experimental data are supplemented by first-principles theoretical calculations of the core-level shifts for a ternary alloy to allow for modeling of the influence of capping materials on the chemical shifts.

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I. INTRODUCTION

Multilayers have attracted interest in many fields because of their numerous practical applications and interesting properties. Nowadays, the development of technology is strongly correlating with the advance of nanodevices, built up by multilayers and thin films or superlattices. The thickness, composition, and interface structure of the layers are used to tailor magnetic, mechanical, and optical properties of the devices. Ni/Cu multilayers are technologically interesting because of the relatively easy growth[1] and of numerous applications. They are, e.g., used in applications related to magneto-optical recording or sensors[2] due to the giant magnetoresistance or underbump metallization to maintain solder wettability in flip chip interconnections.[3] Ni/Cu multilayers have also awakened interest as prototype systems to investigate magnetic properties at ultrathin film scale.[4] Knowledge of the bulk electronic structure of alloys is especially desirable to explain the magnetic properties of both NiCu alloy[5,6] and the ordered compounds.[4,6–8] The idea is that the intermixing at the interfaces changes the local magnetic moments due to hybridization and the effect may be detectable in the total magnetization of the sample.[6] Despite the numerous studies of nanostructured materials, some phenomena such as diffusion and reactions at interfaces are still quite poorly understood and difficult to predict within the ultrathin limit. High kinetic-energy photoelectron spectroscopy (HIKE) has lately attracted large interest and rapidly developed into a promising tool to address electronic properties of buried interfaces and bulk layers,[9–19] as it is one of the few methods that enable nondestructive bulk sensitive studies. The great advantage of HIKE is the accurate measurement of shifts in core-level binding energies of bulk atoms, which reflect changes in chemical environment and give us information about intermixing of interface atoms and alloying of the multilayers. The first HIKE results of Ni/Cu multilayers[20] were combined with theoretical studies and the results convincingly demonstrated the potential of HIKE to study the interface roughening and thus also the alloying process. In these studies the heating was carried out in coarse steps. The resulting Cu $2p_{3/2}$ spectra of Pt capped Ni_5Cu_5 as a comparison to the bulk Cu $2p_{3/2}$ spectra are shown in the Fig. 1.

There are no remarkable changes in the Cu $2p$ spectra measured between 20 and 200 °C. The most obvious changes in the binding energy and in the asymmetry of the line seemed to take place above 200 °C. At 250 °C the spectrum has shifted about 0.2 eV toward lower binding energy when compared to the bulk Cu $2p$. After heating the sample up to 300 °C the shift has become slightly smaller. The small positive shift at lower temperatures as a comparison to the binding energy of bulk Cu $2p$ was consistent with the theoretical model described by a GAUSSIAN distribution func-

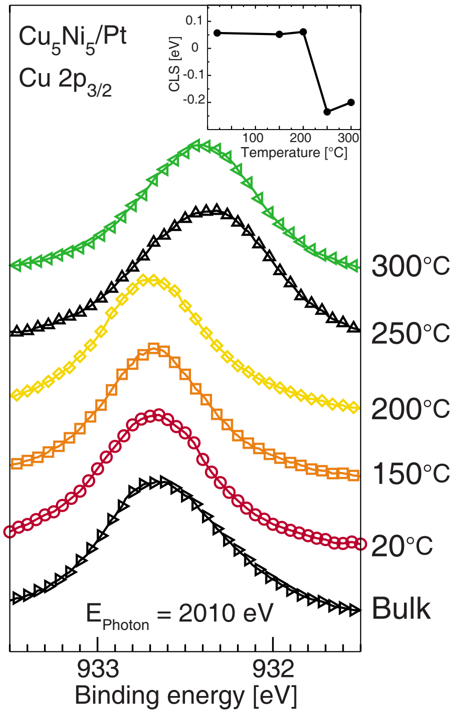

FIG. 1. (Color online) The Cu $2p_{3/2}$ photoemission spectra of Pt capped Ni_5Cu_5 measured using 2010 eV photon energy. A reference spectrum of bulk Cu (100 ML Cu) is included. The inset presents the Cu $2p_{3/2}$ CLS as a function of temperature.

tion with standard deviation Γ.[20,21] It was concluded that these changes are due to the alloying and the distribution of the atoms becoming more homogenous. The inset in Fig. 1 presents the variation of binding energy shift of the Cu $2p$ spectra as a function of temperature. As evidenced by the data, a dramatic change of the core-level binding energy occurs in the narrow temperature range between 200 and 250 °C. As pointed out in Ref. 20 it is essential to perform extended studies to more carefully investigate the intermixing process. The present report extends the previous studies and explores the role of segregation on the opposite shift of the Cu $2p$ level at 300 °C in a more detailed manner. The results are surprising, and further emphasize the strong potential of HIKE. In the analysis of the new data it becomes apparent that besides interface roughening and alloying between Ni and Cu also diffusion of the capping material, segregation of Cu and the effect of heating rate on the intermixing of elements and even on kinetics can be investigated.

II. EXPERIMENTAL

The HIKE experiments were carried out on the HIKE experimental station at the KMC-1 bending magnet beamline in BESSY, Berlin. The beamline is equipped with a high-resolution double-crystal monochromator which consists of three sets of crystals, InSb, Si [111], and Si [422], that can be changed *in situ* within few minutes. The HIKE setup is equipped with a Gammadata Scienta R4000 electron analyzer. The analyzer is modified for high transmission and high resolution at electron kinetic energies up to 10 keV. More detailed information on the experimental set up can be found in Ref. 13. In our experiments most spectra were measured with photon energy 2010 eV where the overall resolution is 0.26 eV. Some spectra were taken using the third order Bragg angle around 6 keV that preserved the high energy resolution but increased the inelastic mean-free path of photoelectrons. With 2010 eV photon energy the sampling depth was estimated to cover approximately two Ni/Cu interfaces. This photon energy was used to gain the best possible energy resolution and statistics within the time limits of the experiments. Using the 6030 eV photon energy the sampling depth increased up to about 7 nm (6–7 interfaces in the case of Ni_5Cu_5/Pt). All the spectra were measured in normal emission.

Three sets of samples were prepared on MgO(001) substrates using UHV-based dc magnetron sputtering. The multilayer structures included a Fe/Pt/Cu seeding buffer layer on top of which the bilayer Ni/Cu fcc (100) unit was repeated.[22] The uppermost Pt or Ni capping layer was grown to protect the sample. The overall geometry of the multilayer structures is the following: $MgO/Fe_{5.6}/Pt_{39.2}/Cu_{45}/[Ni_{8.8}/Cu_N]_n/Ni_{8.8}/X$ (subscripts give the thickness in Å). This study focuses on the samples where Cu film thickness N in the bilayers was 9 or 3.6 Å (5 or 2 ML) while the number of bilayer repeats n was 15 or 21, respectively. The uppermost capping layer X consisted of 10 Å thick film of Pt or 20 Å thick film of Ni. The growth temperature of the seed layer was 150 °C whereas the rest of the film was grown at room temperature. The growth process of Ni/Cu multilayers is considered to be relatively easy because the lattice mismatch between Ni (100) and Cu (100) is less than 3%.[1] Consequently, the effect of relaxation on the binding-energy shifts is very small when compared to chemical shifts. Thus two different thicknesses of the repeated Cu layer, 5 and 2 ML, respectively, were used and also the capping of the samples was varied. The reference spectrum of bulk Cu was obtained from a 200-nm-thick Cu film grown on the same substrate and buffer layer as described above.

In this paper, the studied samples are divided into two groups based on the capping material: in two multilayer samples, a Pt cap was included in the structure to prevent oxidation or other contamination of the sample. In one of the multilayers the Pt cap was replaced by a thicker Ni layer which had the same function. This Ni cap was very gently sputtered away before the measurements. From now on we will refer to the samples as Ni_5Cu_5/Pt, Ni_5Cu_2/Pt, and Ni_5Cu_5 according to the thickness of the repeated Ni and Cu layers (in ML) and the presence or absence of a Pt cap. Controlling the interfacial quality was done by heating the samples up to present temperature between 80 and 530 °C. The difference between heating steps was usually about 20 °C but at higher temperatures we used steps of 50 °C. After heating the samples at a rate of 10 or 15 °C/min to the final temperature, the samples were cooled down close to room temperature at which point spectra were measured.

The energy scale of all the spectra was calibrated by setting the binding energy of Fermi edge to 0 eV. The background was subtracted using a Shirley background.[23] The full width at half maximum was estimated by fitting the spectra with Voigt line shape with fixed Lorentzian width (constant life time) at every temperature.

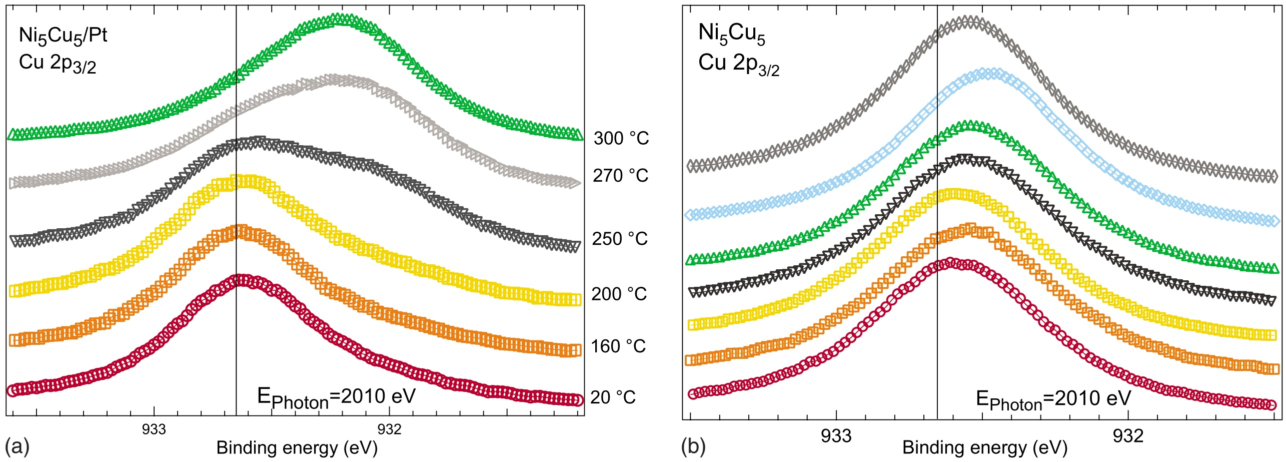

FIG. 2. (Color online) The Cu $2p_{3/2}$ photoelectron spectra of Ni_5Cu_5/Pt (a) and Ni_5Cu_5 (b) measured using 2010 eV photon energy. The black line corresponds the binding energy of bulk Cu $2p_{3/2}$.

III. COMPUTATIONAL METHOD

Core-level shifts are calculated according to first principles utilizing the complete screening picture which includes both initial (ground state) and final (relaxation due to core-hole screening) state contributions in the same computation scheme, all within density-functional theory.[24,25] By using so-called generalized thermodynamic chemical potentials, or ionization energies, μ_i, for a specific core-level i in an atom, the shift is readily given as the difference $\Delta\mu_i = \mu_i - \mu_i^{\mathrm{ref}}$. The reference, μ_i^{ref}, here corresponds to the ionization energy in the pure metal. Note that the chemical potentials are computed from total energies of ground state and core-ionized systems. In our final state calculations the core electron is promoted to the valence band, ensuring charge neutrality and the full screening of the core hole.

In the present work the shifts are calculated for the ternary fcc NiCuPt disordered alloys using a Green's function technique with the atomic sphere approximation, a *spdf*-orbital basis set, and solving the problem of disorder within the coherent potential approximation.[26–28] The exchange-correlation function was set to the local-density approximation, parametrized according to Perdew *et al.*[29] Computations were done in intervals of 10 at. % over the ternary disordered NiCuPt alloys, only using theoretical equilibrium volumes. A more detailed description of the methodology and examples of core-level shifts (CLS) calculations can be found in Refs. 7, 20, 30, and 31.

IV. RESULTS

A. Alloying of Ni_5Cu_5/Pt and Ni_5Cu_2/Pt

One of the central questions in the continuation of the HIKE experiments of Ni/Cu multilayers was the study of more precise behavior in the temperature range between 200 and 300 °C where, according to the first experiments, the most rapid changes occurred. The experiments were begun with Ni_5Cu_5/Pt and Ni_5Cu_2/Pt samples following almost similar heating procedure as before. However, the heating was carried out by using smaller (10–30 °C) steps between 80 and 350 °C. The resulting Cu $2p_{3/2}$ spectra of Ni_5Cu_5/Pt are presented in Fig. 2(a). Similar behavior was observed for the Cu $2p$ binding energy in Ni_5Cu_2/Pt.

Compared to our previous investigation (cf. Fig. 1) a pronounced shoulder is now clearly present already in the spectrum recorded at 200 °C. The intensity of the shoulder keeps increasing as the temperature increases and at 300 °C the peak has shifted about −0.45 eV when compared to the room temperature Cu $2p_{3/2}$ spectrum. This is more than double the shift observed in the first experiments. Also the shape of the Cu $2p$ spectra in Fig. 2(a) is clearly more asymmetric between 200 and 300 °C than it was in the previous studies. The binding energy of the room temperature Cu $2p_{3/2}$ spectrum is very close to the binding energy of bulk Cu $2p_{3/2}$ (932,65). The presented spectra demonstrate unquestionably that the interfaces are destroyed as a result of heating and the sample is better described as an alloy at higher temperatures. However, the almost −0.5 eV shift of Cu $2p$ corelevel and the dramatic changes in the asymmetry of the spectra strongly suggest that we are studying a ternary alloy instead of a binary NiCu alloy. The reported experimental binding energy shift of Cu $2p$ in $Pt_{1-x}Cu_x$ alloys varies between −0.3 and −0.6 eV (Refs. 32 and 33) while it is maximum −0.25 eV in the case of $Ni_{1-x}Cu_x$ alloys.[34,35] Also the Ni $2p$ core-level spectra were measured at each temperature. A most reasonable expectation would be to observe a binding-energy shift caused by alloying also for this case. After careful calibration Ni $2p$ showed at most a −0.1 eV shift between room temperature and higher temperatures. The binding energy of Pt $4f$ level did not change significantly in course of the alloying process. However, some narrowing of the Pt $4f$ photoemission line was observed as a function of temperature and at lower temperatures, some asymmetry was seen on the high binding-energy side of the spectra.

Interface core-level shift

Next we analyzed the Cu $2p_{3/2}$ spectra of Ni_5Cu_2/Pt sample where the bilayers, in an ideal case, should contain only interface Cu atoms. The Cu $2p$ binding energy at room

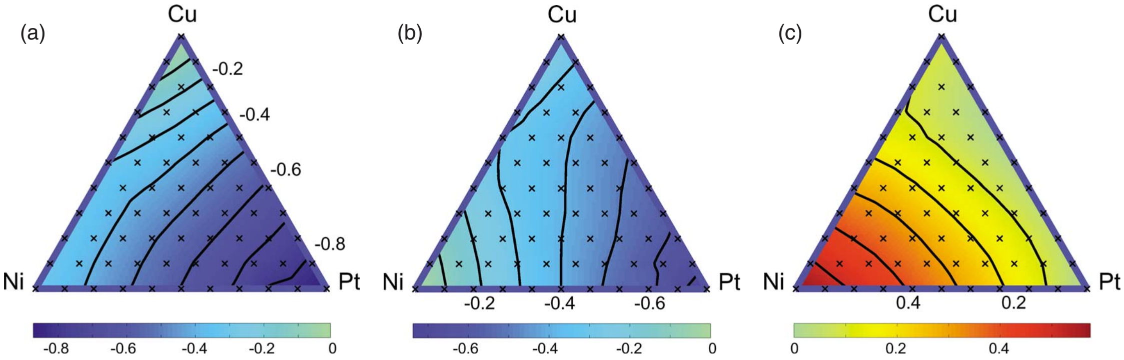

FIG. 3. (Color online) The theoretical core-level shifts of (a) Cu and (b) Ni $2p_{3/2}$ and (c) Pt $4f_{5/2}$ in fcc disordered ternary CuNiPt alloys are shown above. For clarity, the small circles mark incremental differences in 10 at. %. Isolines are plotted in steps of 0.1 eV over the alloy compositions. Note that the sides of the triangles correspond to the respective binary alloys.

temperature was approximately 0.1 eV lower than the binding energy of such spectra of Ni_5Cu_5/Pt sample. At 250 °C a shoulder appears on the low binding-energy side of Cu $2p_{3/2}$ and at 300 °C we observe about −0.4 eV shift. The changes in the asymmetry of the Cu $2p_{3/2}$ spectra of Ni_5Cu_2/Pt are consistent with the results of Ni_5Cu_5/Pt even if the changes in spectral shape and binding energy are not as pronounced as in Ni_5Cu_5/Pt due to lack of bulk Cu atoms in Ni_5Cu_2/Pt. Also the Ni $2p$ and Pt $4f$ spectra of Ni_5Cu_2/Pt were consistent to those of Ni_5Cu_5/Pt. This observation gives an estimate of the interface core-level shift (ICLS) of Cu $2p$ in the situation where four of the twelve nearest neighbors of Cu are Ni atoms and the rest of them are Cu atoms. Since the interface is never strictly perfect on the atomic scale, this 0.1 eV shift can be considered as an average ICLS in a situation where most of the interface is sharp but still some islands exist.

B. Theoretical core-level shifts in disordered NiCuPt alloys

We carry out first-principles calculations of core-level shifts in ternary disordered fcc NiCuPt bulk alloys. Previously, a successful interpretation based on layer-resolved core-level shifts was performed to describe the evolution of interface qualities in CuNi multilayered structures.[20] Here our focus lies on the effectively disordered systems at higher temperatures, with the goal of capturing more general average trends. Therefore, to conduct a qualitative analysis of the experimental findings, it is very useful to compute the shifts in the ternary disordered alloys.

In Figs. 3(a)–3(c) the respective core-level shifts of Cu and Ni $2p_{3/2}$ and Pt $4f_{5/2}$ are shown as a function of the atomic concentrations over the disordered CuNiPt alloys. The triangle sides represent the binary alloys NiCu, CuPt, and NiPt, with results similar to the theoretical shifts reported.[31] First, turning to the Cu core-level shift in Fig. 3(a), it is clear that the more negative shifts indicate a larger concentration of Pt in the ternary alloy, while a smaller shift is obtained for the alloys with high concentrations of Cu and/or Ni. Considering the Ni $2p_{3/2}$ shift in Fig. 3(b), the overall size is smaller in comparison with Cu, though also here larger negative shifts are found in the concentration ranges dominated by Pt. Finally, for the Pt CLS, Fig. 3(c), there is a pronounced difference in the calculated shift between the CuPt and NiPt binary alloy limits, where the results for CuPt remains close to zero in comparison to the larger shifts in NiPt. This difference depending on Cu and Ni concentrations is also found over the ternary alloys. We note that the therotical $4f_{5/2}$ core-level shifts over CuPt alloys reported in Ref. 31 also produce shifts close to zero over the whole concentration range. Further, the shifts are quite sensitive to deviations from the theoretical equilibrium volume. It is important to keep in mind the probing depth when comparing the experiments and calculations. When we are studying Ni_5Cu_5/Pt sample at room temperature with 2010 eV photon energy we measure signal from a layer that covers approximately 5 ML of Pt, 5 ML of Cu, and 5–7 ML of Ni.

C. Ni_5Cu_5 without Pt capping

The obvious way to confirm the formation of a ternary NiCuPt alloy was to repeat the experiments with a sample without Pt capping. We chose to study a Ni_5Cu_5 sample where Pt capping layer was replaced by 2-nm-thick Ni (100) layer. The protective Ni layer was very gently sputtered using small current and short sputtering times. Overview spectra were measured after every cycle and the sputtering was continued until no signature of oxide was found in the Ni $2p$ spectrum. At this point the intensity of Cu $2p$ relative to the intensity of Ni $2p$ increased slightly, consistent with the expectation of removing a surface oxide layer with a thickness of about 3 unit cells. Resulting Cu $2p_{3/2}$ spectra, which were measured with 2010 eV photon energy, are presented in Fig. 2(b). This time more obvious changes were observed also in Ni $2p_{3/2}$ spectra (Fig. 4) at the higher heating temperatures.

Ni $2p$ starts to shift toward lower binding energies at about 200 °C. The shift continues as the temperature rises and alloying goes forward. At 530 °C the Ni $2p_{3/2}$ has shifted about −0.2 eV. The shift at 300 °C is comparable to the results of the Ni_5Cu_5/Pt and references of Ni $2p$ shift in NiCu alloys.[34,36] The calculated Ni $2p$ core-level shift in a NiCu alloy is approximately the same than the experimentally observed shift. The binding-energy shift of Cu $2p$ is still negative but has decreased considerably being maximum −0.1 eV at temperatures between 320 and 400 °C. Now, the shift is 50% smaller than the earlier experiments revealed.[20]

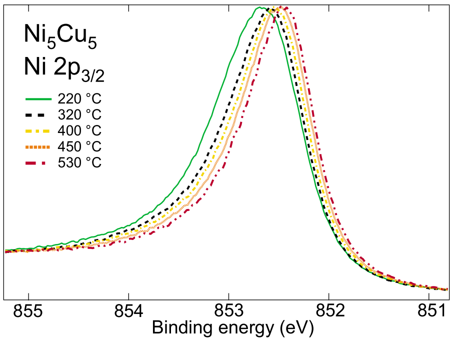

FIG. 4. (Color online) The Ni $2p_{3/2}$ photoelectron spectra of Ni_5Cu_5 measured using 2010 eV photon energy.

It is also interesting that Cu 2*p* starts to shift back toward higher binding energies when temperature reaches 400 °C and is less than −0.05 eV at 530 °C. We can resolve a small shift backward also in the first Cu 2*p* spectra (Fig. 1)[20] but this shift was observed already at lower temperature.

D. Diffusion of Pt cap, segregation of Cu

Analysis of the relative intensities between core-levels (Figs. 5(a), 5(b), and 6) reveal that the most evident changes occur around and above 250 °C.

Based on the Figs. 5(a) and 5(b) the most obvious observation is that the intensity of Cu relative to the intensity of Pt increases in both samples, Ni_5Cu_5/Pt and Ni_5Cu_2/Pt, as a function of temperature. The intensity of Cu relative to the intensity of Pt in Ni_5Cu_5/Pt increases very fast and almost twice us much as in Ni_5Cu_2/Pt between 250 and 270 °C. In Ni_5Cu_2/Pt we see only small changes in the intensity of Cu relative the intensity of Ni. Since the intensities of Cu and Ni relative to the intensity of Pt are increasing approximately at the same rate in a relation to each other, and changes in I_{Cu}/I_{Ni} curve are very small in the Ni_5Cu_2/Pt, we conclude that capping material Pt is diffusing into the layers and intermixing with both Cu and Ni. The intensity of Ni relative to the intensity of Pt increases quite steadily in both samples and intermixing between these compounds seems to start already around 150 °C. On the other hand, the intensity of Cu relative to the intensities of Ni and Pt in Ni_5Cu_5/Pt increases more and faster than the intensity of Ni relative to the intensity of Pt, which suggests that the larger amount of Cu atoms accelerates the Cu segregation to the surface. When the Pt cap is missing the Cu segregation as a function of temperature is easier to observe (Fig. 6). The comparison between the intensity ratios of Cu and Ni in uncapped and Pt capped Ni_5Cu_5 at temperatures below 350 °C shows that the Cu segregation is slightly faster in the presence of Pt.

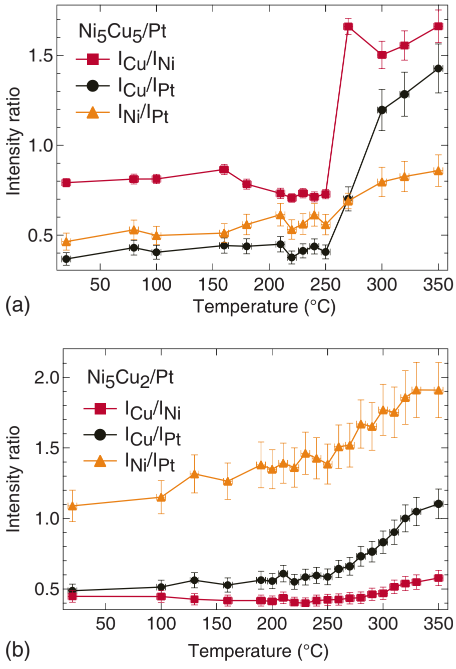

FIG. 5. (Color online) Intensity ratios between Cu 2*p*, Ni 2*p*, and Pt 4*f* corelevels of Ni_5Cu_5/Pt (a) and Ni_5Cu_2/Pt (b).

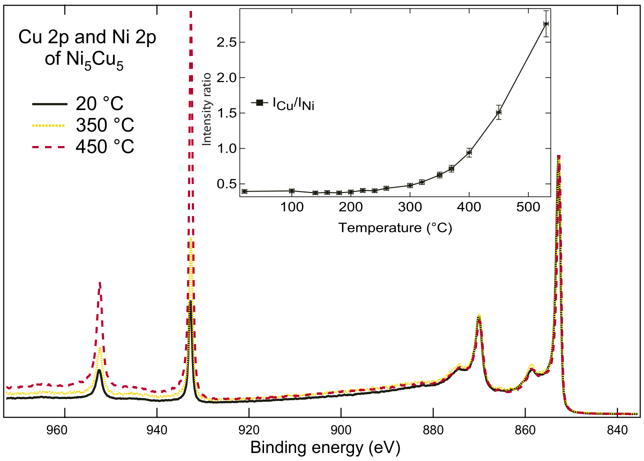

FIG. 6. (Color online) The intensity ratio of Cu 2*p* and Ni 2*p* photoelectron spectra measured at different temperatures using 2010 eV photon energy. The spectra are normalized to a common background before the Ni 2*p* level. The increased intensity of Cu 2*p* relative to the intensity of Ni 2*p* as a function of heating temperature is due to segregation of Cu.

E. Cu 2*p* measured at higher excitation energy

The alloying of Ni/Cu multilayers is well demonstrated by analyzing the core-level spectra measured with excitation energy of 2010 eV. However, with this photon energy we are studying about two interfaces. As shown above (Fig. 6), the contribution to the signal due to Cu segregating to the surface region becomes substantial. Consequently, a set of Cu $2p_{3/2}$ spectra of Ni_5Cu_5 were measured also with a higher photon energy (Fig. 7). An excitation energy of 6030 eV was used to observe the alloying process more similar to the first experiments[20] where the heating procedure was more rapid with fewer temperature steps and narrower temperature range which showed almost no Pt diffusion and Cu segregation in multilayers as a comparison to the data presented in this paper.

The available photon flux at this higher excitation energy is considerably lower than at 2010 eV, making a complete data series at this energy intractable due to time constraints.

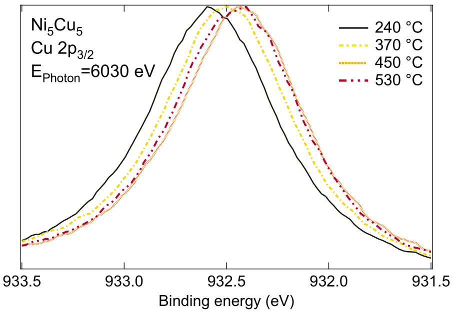

FIG. 7. (Color online) The Cu $2p_{3/2}$ photoelectron spectra of Ni_5Cu_5 measured using 6030 eV photon energy.

To record data at this higher excitation energy and, consequently, higher kinetic energy is however essential as it allows us to investigate the modifications in the multilayer below the Cu rich surface region. As can be seen from Fig. 7, the Cu $2p_{3/2}$ shifts toward lower binding energy having about −0.2 eV shift at 450 °C. This shift is reached at higher temperature than in the first experiments which we suggest are due to differences in alloying process. Latter spectra are contributed by interfaces deeper in the sample where alloying may not be so fast and pronounced as it is closer to the surface. The spectrum measured at 530 °C has slightly shifted backward because of incipient Cu segregation to more layered structure after alloying. These more bulk sensitive measurements give us an estimate of the Cu $2p$ binding energy shift in a NiCu alloy where the concentrations of Ni and Cu are approximately the same and the reorganization starts to have effect on the shifts only at higher temperatures.

F. Two-peak-fit model

In order to investigate the interface roughening in a more quantitative fashion, we attempted a simplified fitting model for Cu $2p_{3/2}$ [Figs. 8(a)–8(c)]. This model is prepared to give an estimate of the rate of alloying and to give a simple picture of the chemical environment of atoms.

The idea of the model is to describe the alloying process by fitting two components in the spectra. The feature on the high binding energy side is due to represent the number of the bulk Cu atoms or Cu atoms that have more other Cu atoms than Ni or Pt atoms as a nearest neighbor (Cu-Cu). Depending on the capping material the other feature is included to represent those Cu atoms that have more Ni (Cu-Ni) or Pt (Cu-Pt) atoms than Cu atoms as a nearest neighbor. The binding-energy shifts between the two-peak-fit compounds are approximately −0.6 eV [Fig. 8(a)], −0.5 eV, and −0.2 eV [Figs. 8(b) and 8(c)] for Ni_5Cu_5/Pt, Ni_5Cu_2/Pt, and Ni_5Cu_5, respectively. We think that it is well, grounded to approximate the progress of alloying using this model because the intensity ratios between the components change as expected as a function of temperature [Figs. 8(a)–8(c), insets]. In Pt capped sample the intensity of low binding-energy component keeps increasing as the alloying proceeds and at higher temperatures majority of Cu atoms are surrounded by Ni or Pt atoms. In the more bulk sensitive spectra

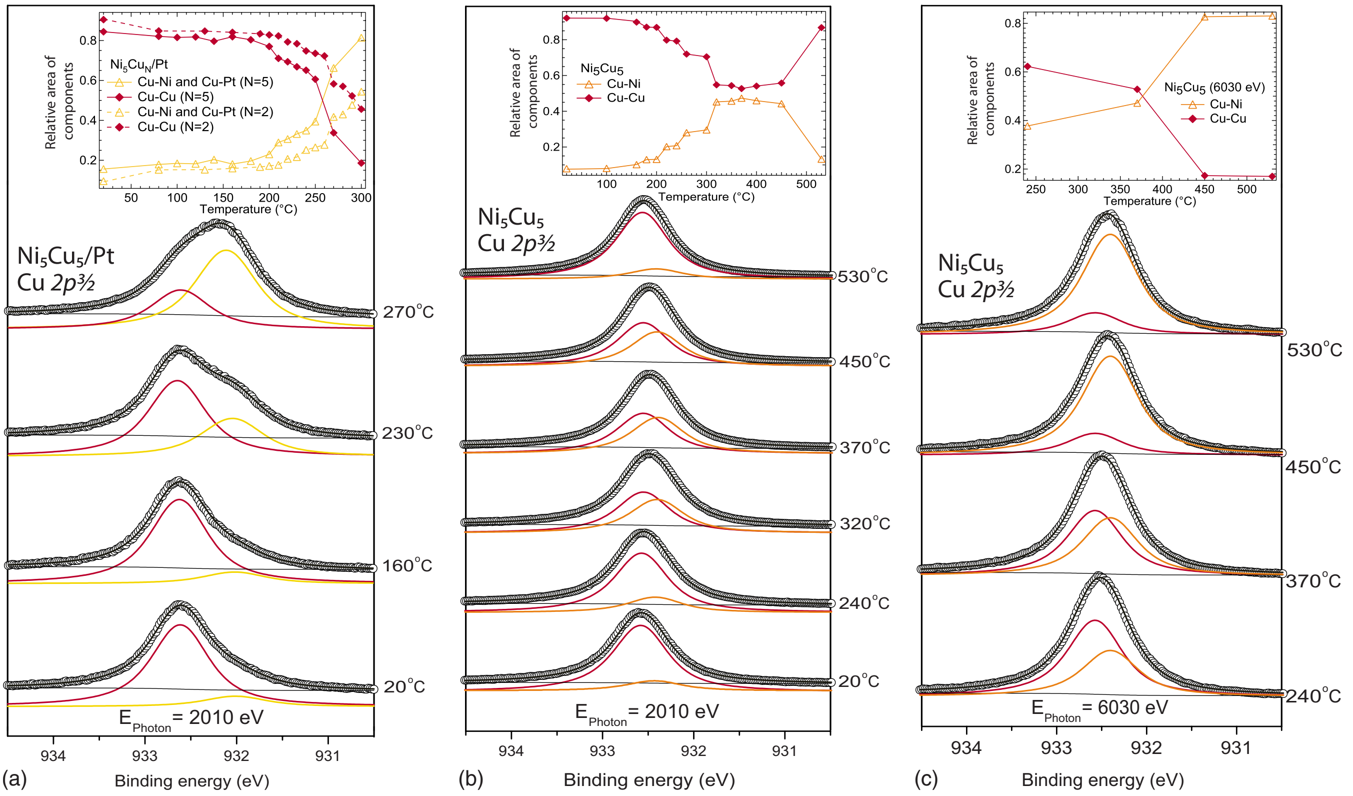

FIG. 8. (Color online) A two-peak-fit model of Cu $2p_{3/2}$ photoelectron spectra of Ni_5Cu_5/Pt and Ni_5Cu_5 at photon energy 2010 eV (a and b, respectively) and Ni_5Cu_5 at photon energy 6030 eV (c). The insets show how the intensity ratio of the two components in the two-peak-fit model of Ni_5Cu_5/Pt, Ni_5Cu_2/Pt and Ni_5Cu_5 changes as a function of temperature.

in Fig. 8(c) of Ni terminated samples the intensity of low binding-energy component increases until 450 °C while in the spectra measured with 2010 eV we observe strong increase in the intensity of high binding-energy bulk Cu component, because of surface segregation of Cu at that temperature. Also the shifts between the two features in every sample seem to follow reasonably well the binding energy shifts found from the literature. When taking into account the resolution of the experiments and the error limits of the fitting parameters it is not reasonable to try to fit own component to signify photoemission from every possible atomic site in the sample but the idea of the model is more like to present the chemical shift between a bulk atom and a dilute atom in an alloy. Especially, we would like to point out the difference between intensity changes in Figs. 8(b) and 8(c). The segregation of Cu, which is known to be very pronounced in the uppermost atom layers[37,38] is not so strong deeper in the multilayers and the spectra measured with higher photon energy (Fig. 8(c)) represent the progress of formation of NiCu alloy where the effect of segregation of Cu is not contributing the binding energy shift as it is in the more surface sensitive case (Fig. 8(b)). The first two sets of spectra are measured using 2010 eV photon energy and the third one using 6030 eV. Alloying can be estimated in a more quantitative way by studying the intensity ratios of the fitted components in the graphs of Figs. 8(a)–8(c) that illustrate how the alloying of Ni_5Cu_5/Pt, Ni_5Cu_2/Pt, and Ni_5Cu_5 proceeds with temperature. The graphs show that the alloying starts around 170 °C in both Pt capped and Ni capped samples but the rate of alloying is affected by three different factors: the presence of the Pt cap, the number of Cu layers, and Cu segregation. When we compare Ni_5Cu_5/Pt and Ni_5Cu_5 it seems that the presence of Pt makes the alloying advance faster. On the other hand the rate of alloying seems to be about the same in Ni_5Cu_2/Pt and Ni_5Cu_5 when 2010 eV photon energy is used. At 300 °C about half of the Cu atoms are in an alloy in Ni_5Cu_2/Pt and Ni_5Cu_5 while in Ni_5Cu_5/Pt the percentages are similar already at 250 °C. On the other hand also the effect of Cu segregation on the rate of alloying is confirmed with the two-peak-fit model. The inset in Fig. 8(c) suggests that that the same level of alloying is reached at 50 °C higher temperature than in the inset of Fig. 8(b) where the segregation is contributing to the observed behavior due to the reduced bulk sensitivity at the lower photon energy.

V. DISCUSSION

As can be seen from the presented results, our HIKE study of Ni/Cu multilayers gives information on the alloying process and the intermixing of capping material, segregation effects, and the influence of heating and thickness of the individual layers in the multilayer on these phenomena. The first observation is that the Pt capped Ni/Cu multilayers form ternary and binary alloys in the course of heating process. Obvious changes in asymmetry and binding energy of Cu $2p$ were observed and the intermixing of Pt with Ni and Cu was convincingly demonstrated. The calculated core-level shifts of NiCuPt alloys presented here support our conclusions related to Pt intermixing with Cu and Ni and provide information on the shifts in ternary alloys. Our observations suggest that Pt diffusion is more pronounced in the environment with more Cu atoms than Ni atoms (cf. Fig. 9). This is supported by the fast changes in intensity ratios of Cu relative to Pt in the Ni_5Cu_5/Pt (Fig. 5(a)) which shows that the number of Cu atoms in the multilayers plays an important role in intermixing. The histograms in Fig. 9 are based on the intensities of the two-peak-fit components of Ni_5Cu_5/Pt and Ni_5Cu_5 measured with 2010 eV photon energy and they present how the chemical environment of Cu atoms changes as a function of temperature. The percentages of CuNi and CuPt alloys can be estimated by comparing the intensity changes of two fitted components in the spectra of these samples. Considering the results presented in the histograms we can also derive more quantitative information on the chemical environment of Ni and Pt atoms. For example, at 240 °C more Ni atoms are in an alloy than Pt atoms. At 300 °C the situation has changed and the Ni layers seem to be more organized.

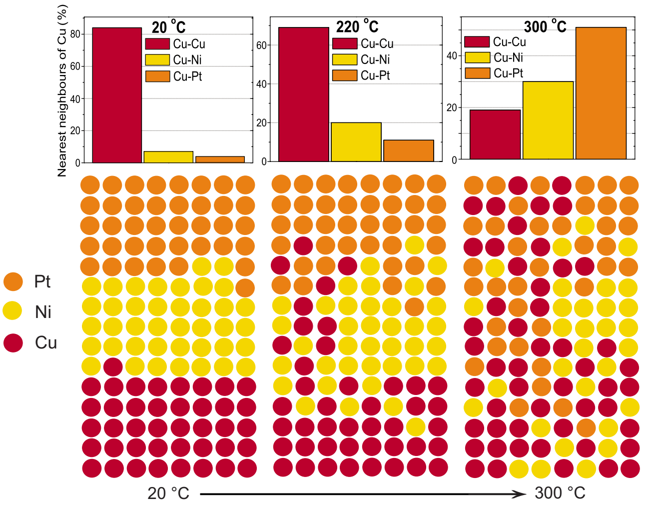

FIG. 9. (Color online) Schematic illustration of intermixing and alloying of Ni/Cu multilayers and Pt cap as a function of temperature. The changes in the chemical environment are described by histograms that are based on the two-peak-fit models of Ni_5Cu_5/Pt and Ni_5Cu_5.

The core-level binding energies in $Ni_{1-x}Cu_x$, $Pt_{1-x}Cu_x$, and $Pt_{1-x}Ni_x$ alloys reported in the literature are also consistent with our experiments. Several experimental binding energy shifts (ΔE_B) have been compiled and are compared to our results. For $Ni_{1-x}Cu_x$ alloys the following binding energy shifts for Cu $2p$ and Ni $2p$ have been measured: $\Delta E_B^{Ni}: 0--0.6$ eV (Refs. 34 and 36):, $\Delta E_B^{Cu}: 0--0.25$ eV (Refs. 34 and 35) as a function of concentration. ΔE_B^{Cu} is close to zero when Cu concentration is higher than 50%. ΔE_B^{Ni} decreases as a function of decreasing Ni consentration. ΔE_B^{Cu} in $Pt_{1-x}Cu_x$ alloys varies between -0.3 and -0.6 eV (Refs. 32 and 33) as a function of decreasing x while ΔE_B^{Pt} stays close to 0 eV.[32,33,39] In $Pt_{1-x}Ni_x$ alloy the ΔE_B^{Ni} changes between 0 and -0.2 eV and ΔE_B^{Pt} between 0 and 0.3 eV as a function of decreasing Ni and Pt concentrations.[40] Studies of Pt on Cu(100) or Cu(111) observe intermixing of Pt and Cu around 300 °C.[41,42] For 0.8–3-ML-thick Ni film on Pt (111) alloying temperature between 450 and 700 K has been reported.[43] The changes in the core-level binding energies and the relative intensities give valuable information on surface roughening and alloying as a function of temperature. When it comes to multilayers it is especially important to pay attention to the changes caused by heating since in the magnetron sputtered Cu/Ni samples the substrate temperature plays an important role in the formation of a superlattice structure. One of the most studied properties of binary alloys has been surface segregation which plays an important role also in the present study. In NiCu alloys the Cu segregation is known to be a pronounced effect since the surface free energy of Cu is significantly lower than that of Ni. The heat of alloy formation is slightly endothermic and Cu segregation is strongly exothermic. According to the x-ray photoelectron forward scattering studies of Ni-Cu-Ni (100) structures the Cu segregation in 1 ML Cu/1 ML Ni sample starts already below room temperature and is a rapid process at about 450 K.[44] It is also known that under equilibrium conditions the surfaces of NiCu and CuPt alloys are enriched in Cu.[45,46] Erdélyi *et al.*[47] have studied the interplay of Ni layer-by-layer dissolution and Cu segregation of finite Ni (111) layers on semi-finite Cu (111) substrate by Auger electron spectroscopy and calculations of concentration profiles. Their reported results of the time evolution of segregation and concentration profiles support our findings on Cu segregation based on the intensity variations and decrease in Cu 2*p* chemical shift at higher temperatures. This study also confirms that the temperature and the concentration of Cu in multilayers have an important role in the kinetics. In our experiments the segregation of Cu toward the surface was evident in the case of Ni capped specimen. We note that our results also allows to address the influence of the total deposited power on the alloying which will ultimately allow direct connections to thermodynamical data. The diffusion of Pt made it more difficult to estimate the segregation in the Pt capped samples, but the results indicate that Cu segregation occurs also for these and that it may have a role on the Pt intermixing as well.

While the present calculations on the disordered ternary alloys are expected to give an estimation of the experimental trends at higher temperatures, it would also be of great interest to perform more detailed theoretical studies. For instance, in a future work, segregation effects in the layered structures could be investigated using Monte Carlo methods, see, e.g.,[48] in order to provide structures as a basis for layer-resolved CLS computations. One can note that so far there have been very few such detailed studies in the literature.

VI. CONCLUSIONS

We have studied Ni/Cu interfaces of multilayer samples with different compositions. The bulk sensitivity and nondestructive character of HIKE method were exploited to observe interface roughening and alloying as a function of heating temperature. Destroying of interfaces and first signs of alloying were seen already at low temperatures which brings valuable information related to sample preparation. Another important result connected especially to multilayer fabrication process is the diffusion of protective Pt capping layer into the sample. Analysis of the core-level binding energies and their intensities relative to each other give versatile information on the physical and chemical phenomena occurring in the multilayers but the exact information about the interface quality is hard to obtain experimentally. Relating to these difficulties we propose a simple two-peak-fit model for Cu 2*p* spectra that can be used to qualitatively and even at some level also quantitatively estimate the interface roughening. The relative intensity variations of core-levels of Cu, Ni and Pt and the compounds of two-peak-fit model of Cu 2*p* as a function of temperature give indicative information about the kinetics of the compound atoms. The experimental study is consolidated by first-principles calculations of core-level shifts in ternary alloys.

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