Room-Temperature Instability of Co/Cu(111)

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The compositional and structural stability of UHV-grown ultrathin cobalt films on Cu(111) are investigated by low-energy ion scattering. Even at room temperature migration of copper substrate atoms onto the cobalt film by surface diffusion occurs during and after the deposition process. The resulting film and interface structure therefore depends critically on deposition rate and temperature as well as on time of measurement. Our findings provide an explanation for the controversial results on structural and magnetic properties of Co/Cu films and multilayers.

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Ultrathin magnetic films and multilayer systems are promising candidates for future magneto-optic storage devices and magnetic read-out systems [1]. Furthermore, they allow one to study such interesting phenomena as two-dimensional magnetism and the recently discovered effects of giant magnetoresistance [2,3] and oscillatory magnetic coupling [4] between magnetic layers, separated by a nonmagnetic spacer material.

Co/Cu films with fcc(111) growth direction provide one of the major systems for the investigation of these effects and are technologically important, due to the large magnetoresistance effect of up to 65% found at room temperature (RT) [5,6]. However, the experimental results concerning the magnetic properties of Co/Cu(111) multilayers are puzzling: Films prepared by sputtering techniques exhibit oscillations of magnetoresistance and magnetic coupling [5,6]. These effects are not or only weakly present in films grown by molecular-beam epitaxy (MBE) [7–12], although the latter are thought to possess a much higher degree of crystalline perfection. The crucial step in the preparation of these multilayers is the growth of Co on Cu. This results in a thermodynamically unfavorable situation, since the surface free energy of Co is higher than that of the Cu substrate [13].

The growth and structure of MBE-grown Co/Cu(111) films have been studied in a number of recent publications [13–19]. Although the same preparation technique was used, these results are also contradictory. While part of the studies find three-dimensional island growth of Co on Cu(111) [13–15], others report a layer-by-layer growth mode [16–18]. In some studies, the presence of Cu atoms on top of the Co islands was suggested [13,15].

Recent publications have stressed the importance of interfacial scattering for magnetic coupling and giant magnetoresistance [20–22]. The structure of the Co/Cu interface therefore deserves special attention. So far both atomically abrupt [23] as well as intermixed and rough interfaces [24,25] have been reported.

We used low-energy ion scattering (LEIS) [26,27] to study the growth and stability of Co/Cu(111) films. This highly surface-sensitive technique provides mass-selective real-space information on the local atomic arrangement at the surface, including surface defects. LEIS is therefore especially suited to investigate the initial stage of growth and the buildup of the interface of Co/Cu(111).

The measurements unambiguously show that Co films are unstable even at RT. With increasing time and/or temperature, a Cu enrichment of the top layer evolves, resulting in interfaces with varying degrees of intermixing, depending on deposition rate, temperature, and time of measurement.

In all experiments, the Cu(111) single crystal was kept at RT (300 ± 5 K) during deposition. Co (purity 99.99%) was deposited at a rate of $\sim$0.25 monolayer (ML)/min from an electron beam evaporator with an integrated flux monitor (Focus EFM3). During evaporation the pressure never exceeded 1.5×10^{-10} mbar. All ion-scattering experiments shown below were recorded using a 5 keV Ne^+ beam incident along the $[\bar{1}\bar{1}2]$ azimuth of the Cu(111) substrate. The scattering angle was set at 165°.

The intensity of backscattered Ne^+ ions as a function of their kinetic energy is shown in Fig. 1. The peaks at 1200 and 1340 eV are due to Ne^+ ions scattered from Co and Cu atoms, respectively. Spectra were recorded at an incidence angle of 40° (measured relative to the surface plane). Only ions backscattered from the surface layer are detected under this condition. The spectra were recorded before as well as 3, 15, 30, 60, and 120 min after evaporation of 1.2 ML of Co. The sample was kept at RT during the whole experiment and the Ne^+ beam was shut off between the measurements. Although more than a monolayer of Co was deposited, a large signal from Cu atoms can be seen in all spectra. This clearly demonstrates that Co does not grow layer by layer, in agreement with many previous studies [13–15]. With increasing time after evaporation, the Co peak at 1200 eV decreases, whereas the Cu signal increases. The variation in the Co peak height is roughly twice that of Cu. This difference is mainly due to the existence of two Cu isotopes, yielding a broader Cu backscattering peak.

The data clearly show that the surface is depleted with Co and enriched with Cu atoms, with increasing time

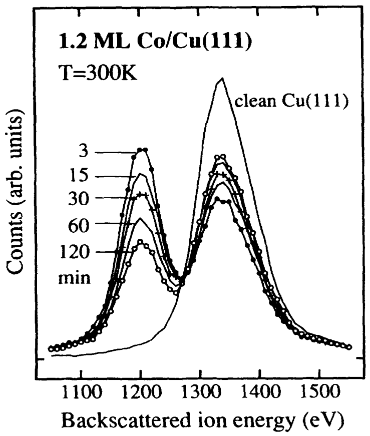

FIG. 1. Ion scattering spectra of Cu(111) and of 1.2 ML Co/Cu(111) at RT. The peaks at 1200 and 1340 eV are due to Ne^+ ions scattered from Co and Cu atoms, respectively. Spectra are recorded under conditions where only the top layer contributes to the scattering signal. Numbers denote the time in minutes elapsed between the end of Co evaporation and the LEIS measurement.

after the deposition process. Three different processes may be responsible for the observed instability of the Co film: (a) sputtering due to the impinging 5 keV Ne^+ ions, (b) adsorption of impurities from the gas phase, or (c) diffusion of Cu and/or Co atoms.

Process (a) was excluded since repeating the experiment with the same number of spectra, and hence the same total fluence of Ne^+ ions within 11 min after evaporation produced changes similar to that of the 15 min spectrum in Fig. 1. Thus the change in the first layer composition depends only on the time after evaporation, but not on the Ne^+ fluence. Measurable sputtering effects also seem quite unlikely, because experiments were carried out with a flux of only 0.002 Ne^+ ions per surface atom per spectrum. Process (b) can also be excluded, since LEIS utilizing 1 keV He^+ ions revealed only minor amounts (<3%) of contaminants (mainly oxygen), even after 120 min. Covering of the Co surface atoms by such small amounts of adsorbates cannot give rise to the observed large decrease of the Co signal (equivalent to $\approx$0.2 ML), nor can it explain any increase of the Cu signal at all. An adsorbate induced rearrangement of the surface also seems unlikely, since adsorbates such as oxygen or CO—instead of destabilizing the surface—usually stabilize thin transition-metal films [28].

Diffusion [process (c)] thus remains as the only explanation. To prove this, two experiments were performed: In the first experiment, again 1.2 ML of Co were deposited at RT. Subsequently, the sample was cooled within a few minutes to temperatures below 200 K, with the final temperature of 140 K being reached after $\approx$30 min. Only minor variations ($\approx$6%) of the Co and Cu signals with time were observed in this case. Cu enrichment therefore is suppressed at low temperatures as expected for a diffusion process. In a second experiment, a linear temperature ramp of 0.5 K/s was applied to a sample covered with 1 ML of Co, while the Co and Cu backscattering signals were monitored. From these signals, the fraction of Co in the first layer was calculated, taking into account a 6% overlap of the Co and Cu signals as well as the sensitivity for backscattering from Co, which—as discussed before—is about a factor of 2 higher than from Cu. In Fig. 2 the Co fraction in the first layer is depicted vs the applied temperature. At 370 K a strong Co depletion of the surface layer is observed. Around 600 K, Co completely disappears from the surface. However, even at RT, the curve exhibits a small but finite slope, proving again that the Co/Cu(111) surface changes its composition. These results clearly demonstrate that the instability of Co/Cu(111) is caused by diffusion of Cu and/or atoms. As the time for the deposition of the 1.2 ML film is comparable to the time scale on which the changes in the Co/Cu ratio occur and as these changes are strongest immediately after evaporation (see Fig. 1), considerable diffusion must already occur during deposition. This will be verified in a later section of the paper. At this stage, several questions remain: Do the compositional changes occur throughout the whole Co film? Are the compositional changes accompanied by morphological and structural changes?

To answer these questions, we used the technique of impact collision ion-scattering spectroscopy (ICISS) [26,27], where the intensities of the Cu peak at 1340 eV and the Co peak at 1200 eV are measured as a function of the angle of incidence Ψ of the ion beam. The resulting intensity variations can be interpreted in a straightforward way on the basis of the shadow cone concept: A first target atom deflects the incoming ion flux in such a way that there is no flux immediately behind it ("shadow cone"). Therefore a head-on collision with a second target atom, as required for scattering angles near 180°, can only occur if this atom is located outside the shadow cone

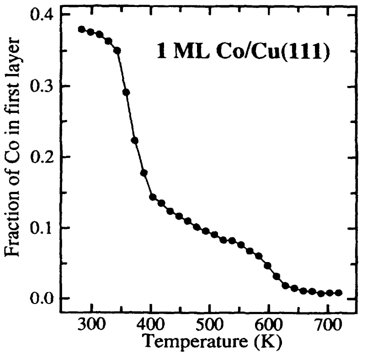

FIG. 2. Fraction of Co atoms in the topmost layer as a function of temperature for 1 ML Co/Cu(111). A heating rate of 0.5 K/s was used.

of the first target atom. Whenever, during the ICISS angular scan, the shadow cone cast by a surface atom is swept across one of its neighbors, a steep rise in the backscattering signal can be observed. This rise is even enhanced by the focusing of the projectile trajectories at the shadow cone edge.

To eliminate considerable diffusion while recording the spectra, the sample was cooled immediately after each of the preparation steps described in the following. The clean surface spectrum [Fig. 3(a)] exhibits two steep intensity rises at critical angles (read off at 50% of the intensity increase) of 11° and 72°. At these angles, the shadow cone cast by a surface atom is swept across its neighbors in the first and second layers, respectively. The respective Ne^+ trajectories Ψ_1 and Ψ_2 are depicted in Fig. 3 (inset), which shows a cut through the crystal along the scattering plane. Almost no backscattering occurs near grazing incidence ($\Psi = 0$), as expected for a flat surface, where each surface atom is hidden in the shadow cone of the neighbor atom. Figures 3(b) and 3(b′) display ICISS spectra for backscattering from Cu and Co atoms, respectively, after deposition of 1 ML of Co. The Co spectrum exhibits the same main features as the clean Cu spectrum in Fig. 3(a). In particular, a well-developed peak can be seen near $\Psi = 72°$. This results from a considerable amount of Co atoms in the second layer, again indicating that Co does not grow layer by layer. This is also evident from the Cu spectrum of the as-deposited film [Fig. 3(b)]. Relative to the clean spectrum, both of the intensity rises at 11° and at 72° are attenuated, which is most clearly brought out in the difference spectrum in Fig. 3(d), which exhibits both a first and a second layer peak. Closer examination of spectra tells even more about the growth process. The Co spectrum in Fig. 3(b′) shows a small intensity increase at $\Psi = 48°$. This is due to Co atoms in the second layer, but with a stacking fault occurring between the first and second layers. Furthermore—in contrast to the clean surface—considerable intensity is observed near grazing incidence. This is attributed to Co atoms at upward steps, such as atoms at island boundaries ("surface defects"—see trajectory Ψ_0 in Fig. 3 inset). The Cu signal [Fig. 3(b)] near grazing incidence also increases upon Co deposition, indicating Co-induced formation of Cu surface defects. Cu diffusion has therefore already taken place during Co deposition, as was already argued before. The peak near $\Psi = 25°$ in Fig. 3(b) results from focusing by surface defects at downward steps down onto atoms of the Cu substrate (trajectory Ψ_2' in Fig. 3 inset [29]).

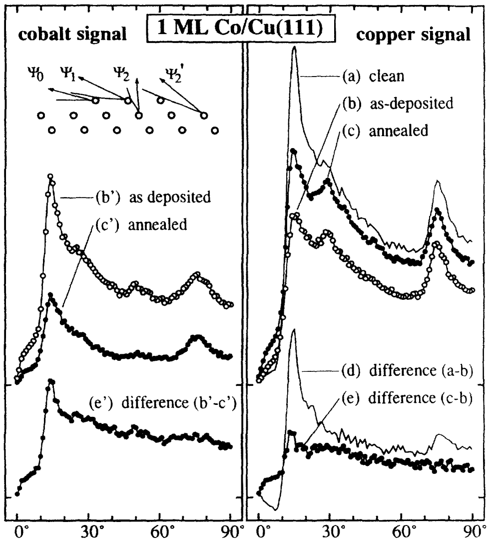

FIG. 3. ICISS spectra of Cu(111) and 1 ML Co/Cu(111). Left (right) panel: Ne^+ ions are backscattered from Co (Cu) atoms. Inset: cut through the Cu(111) crystal along the scattering plane.

In the final preparation step, the sample was annealed, as described before, up to a temperature where the Co fraction of the surface has dropped to ≈12%. Other experiments where the Co depletion was achieved by keeping the sample at RT for 120 min instead of annealing gave similar results. ICISS spectra obtained after the Co depletion are shown in Fig. 3(c) and 3(c′). The changes relative to the spectra before the annealing step are best visualized in the difference spectra. Both the Cu [Fig. 3(e)] and the Co [Fig. 3(e′)] difference spectrum exhibit mainly a first-layer peak at $\Psi = 11°$. No clear second-layer feature can be detected. The Cu enrichment thus predominantly takes place in the surface layer. This finding is most easily explained by formation of a Cu monolayer on top of the deposited Co film, in agreement with Refs. [13,15], where Co islands with Cu atoms on top were suggested. However, no time-dependent changes were reported in these works. Formation of this overlayer is probably due to Cu surface diffusion. Because, first, bulk diffusion is not expected near RT [30] and second, the RT instability is strongest at coverages up to ≈1 ML, where the surface layer after deposition consists of more than ≈60% Cu, whereas the instability is almost absent for coverages above 3 ML, where more than 80% of the surface is covered by Co.

The Cu signal near grazing incidence increases upon annealing, whereas the respective Co intensity decreases. This is as expected for formation of a Cu overlayer, because the Cu atoms, which cover the top and probably also the "shores" of the Co islands, form additional surface defects. If the diffusing Cu atoms do not come from substrate steps (which may be quite far away), but emerge from flat parts of the original substrate surface, holes may appear on the surface, whose perimeter atoms also contribute to the Cu defect intensity. Such Co-induced holes were indeed observed in a recent scanning tunnel microscope (STM) work [14]. Finally, it should be mentioned that the observed critical angles in Fig. 3 do not change upon annealing, indicating constant interatomic distances. However, the Co peak at 48° decreases in intensity [Fig. 3(c′)], revealing a smaller amount of stacking faults between the first and second layer.

In summary, we have observed that ultrathin Co films on Cu(111) are unstable, even at RT. Cu substrate atoms migrate to the surface, trying to form a capping overlayer on top of the Co islands. Such a sandwich structure is energetically more favorable than a Co-covered surface if the energy gained by terminating the surface with Cu is larger than the energy needed to produce a second Co/Cu interface. At RT, Cu diffusion occurs on the time scale of a typical MBE experiment (i.e., several minutes). Therefore, surface composition and also stacking sequence between first and second layer depend not only on preparation conditions but also on the time elapsed between evaporation and measurement, making a comparison of different studies extremely difficult. As the relevant diffusion mechanism is surface diffusion of Cu, migration of Cu will stop once enough Co has been deposited to cover the surface for the most part, leaving behind an intermixed interface. The degree of intermixing depends sensitively on deposition rate and temperature. Assuming that for coverages below 1 ML all Co atoms residing in subsurface layers are covered by Cu, we estimate that to keep intermixing below 1% of a ML a deposition rate of >30 ML/min has to be used at RT. This value is readily obtained by sputtering techniques which therefore produce an abrupt Co/Cu interface, whereas preparation by MBE techniques with their 1 to 2 orders of magnitude lower deposition rate results in an intermixed interface. As interfacial scattering is of great importance for magnetic coupling and giant magnetoresistance [20–22], different magnetic properties are to be expected for MBE and sputter-grown films. Furthermore, according to Ruderman-Kittel-Kasuya-Yosida (RKKY) theory, the conduction electrons transmitting the magnetic coupling are especially sensitive to lateral defects and inhomogeneities in a Cu(111) splacer layer, since—in contrast to other low-index faces of Cu—their group velocity is not parallel to the surface normal [31]. As shown above, such defects occur preferentially in MBE-grown films.

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