Stress and structure in MnCu(001) surface alloys

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The structure and the chemical composition of surfaces and interfaces determine the physical and chemical properties of many film systems where the thickness is of the order several atomic layers. A surface also offers unique possibilities for intermixing between different atoms, even for elements which are immiscible in the bulk. The resulting surface alloy formation leads to a modification of both geometric structure and chemical composition, and significant changes of the physical properties result. An important example is the Mn-Cu system, where different surface alloy structures can be prepared depending on the growth conditions [1].

The impact of surface alloy formation on surface stress is not understood yet. State of the art calculations suggest that details of the alloy induced surface rumpling are decisive for the resulting stress change [2]. To elucidate this new field in more detail we studied the correlation between surface alloy formation and surface stress. We have employed a novel combination of established techniques, namely surface x-ray diffraction (SXRD), and stress measurements by the crystal curvature technique [1].

Figure 1 shows the measured surface stress change, $\Delta \tau_s$, during deposition of Mn on Cu(001) at 420 K. Three stress regimes (I),(II), and (III), are identified by different slopes of the stress curve. In regime (I), the compressive surface stress increases in proportion to the Mn coverage up to 0.5 ML Mn, where the first kink of the stress curve is observed. In regime (II), a continuation of compressive stress, albeit with reduced slope, is found. A second kink in the stress curve at $-2.3$ N/m for 1.3 ML Mn marks the transition to regime (III). In regime (III) no further significant stress change is measured for ongoing Mn deposition. The corresponding surface structures are characterized by their low energy electron diffraction (LEED) patterns, shown in the upper panel of Fig. 1. A c(2x2) LEED pattern is observed for regimes (I) and (II) although with different spot intensities. This indicates that the c(2x2)-superstructure is stable up to 1.3 ML. At higher coverage (regime III) a p2gg(4x2) pattern [3] is observed characterized by faint spots in addition to the strong c(2x2)-spots.

The c(2x2) pattern indicates the formation of a surface-alloy superstructure, where every other Cu surface atom is replaced by a Mn-atom. This structure has been intensively studied before [4], but no structural details are known for the p2gg-(4x2) superstructure [3]. The formation of compressive surface stress in regimes I and II can be attributed to the insertion of the larger Mn atom into the Cu layers. A recent theoretical study suggests that the magnitude of the measured compressive stress
can be ascribed to the Mn-induced relief of tensile surface stress of Cu(001) [2].

We performed surface x-ray diffraction (SXRD) experiments at the European Synchrotron Radiation Facility (ESRF) at beamline ID03 to clarify the p2gg(4x2)-structure of regime III. The structure model which describes the diffraction data best is shown in Fig. 2.

The superstructure is characterized by a compositionally graded two-layer alloy. This differs significantly from the c(2x2)-alloy, where Cu and Mn occupy the surface sites evenly. Our analysis suggests concentrations of about Mn\(_{0.6}\)Cu\(_{0.4}\) and Mn\(_{0.3}\)Cu\(_{0.7}\) for the first and second layer, respectively. As compared to the c(2x2)-phase, where only the top layer is alloyed, this indicates a considerable structural reorganisation upon formation of the p2gg-(4x2) phase, where a main characteristic is the dealloying of the second layer.

The presence of Mn in two layers induces a lateral shift of atoms out of the bulk positions. This leads to a doubling of the lattice parameter along [1\(\bar{1}\)0] as compared to the c(2\times2) structure. Figure 2 shows a wave-like modulation pattern, which offers an explanation for previous scanning tunneling microscopy images [3].

The evolution of the MnCu alloy is schematically summarized in Fig. 3. Continued Mn deposition beyond 0.5 ML coverage leads to Mn-Cu intermixing in the two topmost layers. We propose a de-alloying of the second layer, which is mediated by an inter-layer atomic exchange mechanism, where Mn-atoms from the second layer replace Cu-atoms in the top layer.

Our investigation has revealed that considerable structural transitions accompany the alloy formation. The combination of stress and SXRD measurements is a powerful tool to detect and analyze these structural transitions at surfaces. The Mn-induced compressive stress of the c(2x2) alloy can quantitatively be ascribed to the relief of the tensile surface stress of Cu(001).

References


