Long-Range Chemical Interaction in Solid-State Synthesis: The Formation of a CuAu Alloy in Au/β-Co(001)/Cu(001) Epitaxial Film Structures

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The effect of an inert Co layer (0, 210, 480 nm) on the chemical interaction between Cu and Au in Au/β-Co(001)/Cu(001) epitaxial films has been investigated by X-ray diffraction, nuclear magnetic resonance, photoelectron spectroscopy, and magnetic structure measurements. Mixing at interfaces in Cu/β-Co(001) and Au/β-Co(001) bilayer films has not been revealed up to a temperature of 600°C. The solid-state synthesis of ordered CuAu| and CuAu‖ phases occurs through the Co inert buffer layer in Au/β-Co(001)/Cu(001) trilayer film systems with an increase in the annealing temperature. The initiation temperatures of the CuAu| and CuAu‖ phases increase only slightly with the thickness of the Co buffer layer. The assumption of the long range of the chemical interaction between Cu and Au through the chemically inert Co layer is justified using the performed investigations.

INTRODUCTION

Atomic migration plays a central role in many processes at the nanoscale, but information on its mechanisms and scenarios at low temperatures, which are particularly important for understanding of the physical properties and fundamental phenomena in low-dimensional structures [1], is scarce. The nature of fast diffusion in multilayers and nanostructures in solid-state reactions determines the atomic structure of the reaction products and remains to be widely discussed. Any complete explanation of the formation of the reagents of only one (first) phase and the phase sequence at the interface is absent, although many phenomenological models were proposed in [2]. This is primarily because the structure of even the simplest crystals with a known chemical composition cannot be predicted by ab initio consideration [3]. Diffusion through the grain boundaries and dislocations is the only mechanism underlying the explanations of solid-state reactions. Solid-state reactions in metallic multilayers and nanostructures proceed at low (100–500°C) temperatures at which the 3D diffusion coefficient is very small ($D < 10^{-20}$ cm^2/s) and cannot explain atomic transfer through a film thickness of 100 nm for a characteristic annealing time of 1 h. At present, it is commonly accepted that atomic transfer occurs through the grain boundaries and dislocations with the diffusion coefficient $D < 10^{-13}$ cm^2/s [4]. However, such a mechanism explains only atomic transfer to a distance of 100 nm without migration inside the grains.

The previous investigations show that mixing in Au/Cu film systems begins at low temperatures of about 250°C and leads to the formation of CuAu, Cu$_3$Au, and Cu$_3$Au$_2$ phases [5]. The initiation temperature T_0 of the solid-state reaction in Au/Cu(001) epitaxial systems, which was determined from the temperature dependence of the electric resistance, was $T_0 = 240°C$. The absence of mixing at the Au/Cu interface below the initiation temperature $T_0 = 240°C$ is worth noting [6]. However, the fast mutual migration of Au and Cu atoms over the entire thickness of the Au/Cu(001) sample above T_0 gives rise to the solid-state synthesis of the ordered tetragonal and orthorhombic CuAu phases. The analysis of the solid-state reactions in thin films shows that reactions in Au/Cu samples are associated with the existence of the order−disorder transition in the Cu−Au system and the initiation temperature T_0 coincides with the minimum temperature T_K (Kurnakov point) of the order−disorder phase transition ($T_0 = T_K = 240°C$) [6].
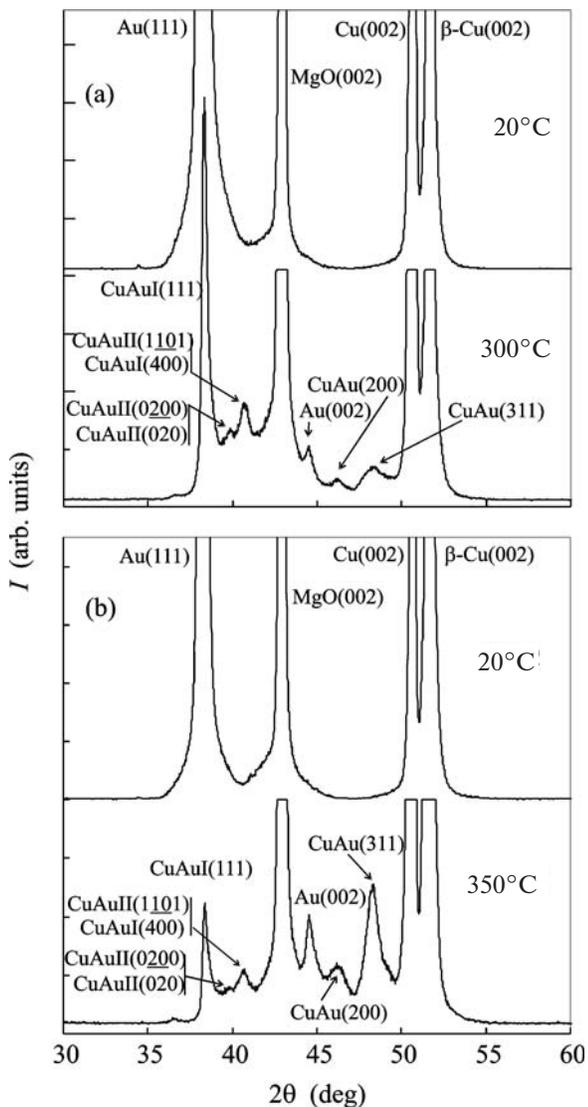
Fig. 1. Diffraction patterns of the Au/β-Co(001)/Cu(001) epitaxial film system in the initial state and after the solid-state synthesis of the CuAu| and CuAu|| phases with the β-Co inert buffer layer with the thicknesses (a) 210 and (b) 480 nm.

As is known, the interatomic interaction potentials describing the chemical bond in metals and alloys are short-range potentials and decrease at distances exceeding the lattice parameter. Therefore, reacting atoms spaced at a distance of several monolayers should not chemically interact with each other. The suppression of solid-state reactions is performed by the sedimentation of chemically inert buffer layers (diffusion barriers) between reacting films. However, the diffusion barriers often do not prevent the mixing of reacting layers [7, 8] and even stimulate the formation of epitaxial reaction products [8].

In this paper, we report the experimental results of the investigation of the chemical interaction between the Cu and Au films separated by the inert Co layer

with a thickness of 210 and 480 nm. The analysis of the results clearly proves that Cu and Au atoms chemically interact above the initiation temperature through the inert Co layer at a distance that is about $\sim 5 \times 10^3$ times larger than the length of the usual chemical bond.

SAMPLES AND THE EXPERIMENTAL PROCEDURE

The experiments were performed with Au/β-Co(001)/Cu(001) epitaxial films obtained using the thermal evaporation method in a vacuum of 10^{-6} Torr by the successive deposition of Cu, Co, and Au layers onto the freshly cleaved MgO(001) surface. The Cu and Co layers were deposited at 250°C and grew directionally. The Au layer was deposited at 200°C and grew in two dominant directions Au(111) and Au(001) (see Fig. 1). The thicknesses of the Au and Cu layers are 100 and 150 nm, which is close to an Au : Cu atomic ratio of 1 : 2. The thicknesses of the Co diffusion barriers were 210 and 480 nm. For comparison, we also used Au/Cu(001) samples without any diffusion barrier. The initial samples were successively annealed for 20 min from 250 to 600°C with a step of 50°C. The appearing phases were identified using X-ray diffraction studies on a DRON-4-07 diffractometer (CuK_α radiation). The surface composition was analyzed with an X-ray photoelectron spectrometer (SPECS GmbH). The spectra were recorded after the cleaning of the surface by an Ar^+ ion beam (5 kV, 30 μA) for 2 min. The structure of the Co layer was studied by the nuclear magnetic resonance method (nuclear spin echo). The X-ray fluorescence spectrum method was used to determine the chemical composition and thickness of the films. The magnetic crystallographic anisotropy K_1 and the saturation magnetization M_S were measured using the torque method with a maximum magnetic field of 18 kOe. The measurements were performed at room temperature.

EXPERIMENTAL RESULTS

In the first series of the experiments, the conditions of the thermal stability of the Co/Cu and Au/Co interfaces were analyzed. To this end, the β-Co(001)/Cu(001) and Au/β-Co(001) samples epitaxially grown on MgO(001) were annealed up to a temperature of 600°C. The diffraction patterns of the initial film systems contained strong β-Co(002), Cu(002), Au(002), and Au(111) reflections. New reflections did not appear after annealing and β-Co(002), Cu(001), Au(002), and Au(111) reflections changed only slightly. The β-Co(001) layer for both samples had a first magnetic crystallographic anisotropy constant $K_1 = -(8-9) \times 10^5$ erg/cm³, which is close to the value in bulk samples [9], and orientation relations [100],(001)β-Co [100],(001)Cu with the Cu layer and [100],(001)β-Co [100],(001)MgO with the

MgO substrate. The magnetic crystallographic anisotropy constant K_1 and saturation magnetization M_S of the β-Co(001) layers in the β-Co(001)/Cu(001) and Au/β-Co(001) samples were independent of the annealing temperature. These results clearly indicate the absence of atomic mixing at the Co/Cu and Au/Co interfaces under annealings up to a temperature of 600°C.

In the second series of the experiments, the Au/β-Co(001)/Cu(001) epitaxial trilayer samples with the inert buffer Co layer with thicknesses $d_{Co} = 0$, 210, and 480 nm were successively annealed to the initiation temperature of the solid-state reaction between the Au and Cu films. The Au/Cu(001) samples with $d_{Co} = 0$ (without Co layer) annealed at a temperature of 250°C exhibit diffraction reflections from the ordered tetragonal CuAu| and orthorhombic CuAu|| phases. These data (not presented here) repeat the results from [6], where it was shown that the solid-state reaction between Au and Cu starts at the initiation temperature $T_0 = 240$°C coinciding with the minimum Kurnakov temperature of the Cu−Au system. The diffraction patterns of the reacted Au/β-Co(001)/Cu(001) samples with the diffusion barrier of the Co layer ($d_{Co} = 210$ and 480 nm) also indicate the CuAu| and CuAu|| phases with the same orientations as the samples without any Co layer (see Fig. 1). Therefore, the diffusion barriers with $d_{Co} = 210$ and 480 nm do not suppress the solid-state reaction between Au and Cu, but increase the initiation temperature $T_0(d_{Co} = 210$ nm$) \sim 300$°C (see Fig. 1a) and $T_0(d_{Co} = 480$ nm$) \sim 350$°C (see Fig. 1b).

X-ray photoelectron spectra of the Au/β-Co(001)/Cu(001) films with the barrier-layer thickness $d_{Co} = 480$ nm after annealing at a temperature of 350°C (see Fig. 2) contain copper lines corresponding to a Cu $2p_{3/2}$ binding energy of 932.8 eV, as well as the Cu $L_3M_{4,5}M_{4,5}$ Auger line with an energy of 918.0 eV. Taking into account that shake satellites are almost absent in a binding energy range of 940−946 eV, these lines can be attributed to metallic copper or Cu and Au compounds. The latter is in agreement with the fact that the Au $4f_{7/2}$ binding energy equal to 84.4 eV is 0.4 eV larger than that for metallic gold. The Cu/Au atomic concentration ratio calculated taking into account the difference between the photoelectron emission depths after ion etching is about 0.7. This confirms the formation of the CuAu phase taking into account that some amount of unreacted Au remains in the sample (see Fig. 1). The presence of cobalt lines implies the partial mixing of the formed CuAu layer with the upper part of the Co layer.

The analysis of the nuclear spin echo spectra confirms that the barrier layer in the Au/β-Co(001)/Cu(001) trilayer films is predominantly in the β-Co(001) phase. The nuclear spin echo spectra of the β-Co(001) layer before and after the synthesis of
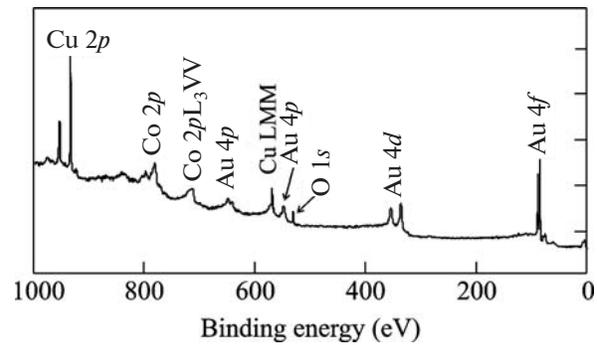
Fig. 2. X-ray photoelectron spectrum of the Au/β-Co(001)/Cu(001) epitaxial film system with the 480-nm Co inert buffer layer after annealing at 350°C.

the CuAu| and CuAu|| phases remain unchanged and the saturation magnetization M_S, as well as the magnetic anisotropy constant K_1, decreases only slightly. A simultaneous decrease in M_S and K_1 (by ~6%) is attributed to the formation of nonferromagnetic cobalt oxides or gold and copper solid solutions based on cobalt. These data indicate that the reacting Cu and Au atoms do not destroy the β-Co(001) epitaxial buffer layer during migration.

DISCUSSION OF THE RESULTS

It is well known that Co does not mix with both Au and Cu. The above experimental results clearly confirm the absence of mixing at the Au/Co and Co/Cu interfaces up to a temperature of 600°C and are in agreement with the data, according to which the mutual diffusion of Co and Cu atoms begins only above 900 K [10] and the annealing of Au/Co multilayers to 300°C does not lead to mixing [11]. However, the addition of the upper Au layer to the β-Co(001)/Cu(001) bilayer film system and the formation of the Au/β-Co(001)/Cu(001) film significantly changes the situation under annealing. Independent of the Co buffer layer, Cu atoms migrate through it, undergo a solid-state reaction with Au, and form the CuAu| and CuAu|| phases. In other words, the Au layer initiates the atomic exchange of Cu with the β-Co buffer layer. The presented results are in good agreement with the data from [4], where Cu and Au atoms in the Cu/Co/Au polycrystalline film system diffuse through the inert Co barrier and form AuCu, Cu$_3$Au, and Cu$_3$Au$_2$ compounds. These data propose a new concept of the nature of atomic transfer through the diffusion barrier or the layer of a product of solid phase reactions. The driving factor of atomic exchange is a strong chemical interaction, which appears above the initiation temperature between Au and Cu atoms through the β-Co inert layer and initiates the synthesis of the CuAu| and CuAu|| phases, rather than random diffusion walk. Since Au and Cu atoms do not chemi-

cally interact with Co atoms, it is natural to assume that the chemical interaction between Au and Cu atoms extends through the 480-nm Co inert layer; i.e., the radius of the chemical interaction is about $\sim 5 \times 10^3$ times larger than the length of a usual chemical bond in metals. This result is very surprising, because the spacing of reacting Cu and Au layers at a distance of 480 nm should lead to the complete suppression of synthesis. The preliminary investigations give an unprecedented result: even a 2.5-μm Co layer does not suppress the formation of the CuAu alloy and only increases the initiation temperature up to 600°C.

The independence of the solid-state synthesis of the CuAu alloy on the Co-layer thickness implies that nondiffusion scenarios of atomic transfer can dominate at the initial stage of the solid-state synthesis. Two factors contradict the classical random diffusion mechanism (through grain boundaries and dislocations) of the transfer of Cu and Au atoms through the inert Co barrier.

1. The threshold character of the solid-state synthesis. Even for bilayer Au/Cu(001) samples without any Co barrier layer ($d_{Co} = 0$), the mixing of the Au and Cu layers and the formation of the CuAu| and CuAu|| phases start only after reaching the initiation temperature T_0 coinciding with the temperature of the order−disorder phase transition (Kurnakov point) in the CuAu layer [6]. The initiation temperature for Au/β-Co(001)/Cu(001) samples increases only slightly with the thickness of the Co layer. The analysis of magnetic measurements indicates that the diffusion coefficient increases by a factor of more than $10^6 - 10^7$ and reaches high values ($\sim 10^{-10}$ cm^2/s) with increasing temperature above the initiation temperature T_0. This is inconsistent with the Arrhenius temperature dependence of the diffusion coefficient.

2. Photoelectron spectroscopy shows that the upper layers in the Au/β-Co(001)/Cu(001) samples after the reaction contain about 40% of Cu irrespective of the thickness of the Co buffer layer. Therefore, a significant part of atoms of the Cu layer, which is necessary for the formation of equiatomic CuAu| and CuAu|| alloys, migrates to the Au layer. This is inconsistent with the random walk of atoms in which most Cu atoms should remain in the Co barrier layer and the content of Cu in the upper layers should be insignificant and decrease with an increase in the thickness of the Co barrier layer.

Owing to these facts, we can state that the migration of reacting atoms in the presence of a chemical interaction is directional and cooperative and ensures their fast transfer to the reaction zone through the buffer layer or reaction product layer. It is worth noting that the atomic transfer of Cu and Au atoms does not give rise to the disordering of the β-Co(001) epitaxial layer. This is possible under the assumption that the migration of reacting atoms occurs through single channels rather than on the entire surface of the barrier β-Co layer. Such channels can be pinholes often existing on the surface of reacting films [12].

Argumentations of the atomic transfer of reacting atoms through the inert buffer layer in the presence of a chemical interaction were proposed previously, but were not further developed. In particular, it was shown that the oxidation of metals is the main driving factor of the diffusion of Fe, Ni, Co [13], and Cr [14] through the 300-nm chemically inert Au layer.

Recently, we demonstrated the long-range chemical interaction between Ni and Fe films separated by a 900-nm Ag inert layer [15]. This implies the presence of a long-range chemical interaction in many trilayer metallic systems. For this reason, investigations of atomic transfer through buffer barriers with various electronic structures are necessary for better understanding of the scenarios and mechanisms of solid-state reactions at the nanoscale level.

CONCLUSIONS

The solid-state synthesis of CuAu| and CuAu|| phases through the chemically inert Co layer in Au/β-Co(001)/Cu(001) epitaxial films has been investigated by X-ray diffraction, nuclear magnetic resonance, photoelectron spectroscopy, and magnetic structure measurements. The absence of mixing of Cu with Co and Au with Co and the formation of the CuAu alloy from the Cu and Au layers separated by the 480-nm chemically inert Co layer clearly prove the existence of a long-range chemical interaction between Cu and Au atoms. A new concept of the nature of atomic transfer has been developed, according to which the main driving factor of atomic migration through the chemically inert barrier layer or the reaction product layer is the chemical interaction between reacting atoms rather than random diffusion mechanism as assumed now.

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