

Long-Range Chemical Interaction in Solid-State Synthesis: The Kirkendall Effect and Solid-State Reactions in Cu/ β -CuZn and Cu/Fe/ β -CuZn Film Systems

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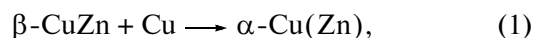
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The results of the experimental investigations of the solid-state reaction of Cu with β brass, which is associated with the Kirkendall, in Cu/ β -CuZn and Cu/Fe/ β -CuZn film systems are reported. It has been shown that the initiation temperature of the solid-state synthesis of α brass at the Cu/ β -CuZn interface is about 200°C. The chemically inert Fe barrier layers 420 and 850 nm in thickness between the Cu and β -CuZn films do not suppress the solid-state synthesis of the α brass, but increase the initiation temperature to about 250°C. This behavior indicates that the chemical interaction between the Cu and Zn atoms through the chemically inert Fe layer is long-range. The X-ray photoelectron investigations reveal the migration of Zn atoms from the β -CuZn layer through the Fe barrier to the Cu layer. The results are interpreted under the assumption that the migration of Zn atoms in the Kirkendall is initiated by the strong chemical interaction between the Cu and Zn atoms in the Cu and β -CuZn layers, which is due to the synthesis of α brass, rather than by the diffusion random walk, as is commonly accepted at present.

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INTRODUCTION

The exclusive role of the Kirkendall in the development of the current approaches to diffusion in solids is well known. In Kirkendall experiments, the diffusion of Cu and Zn in composites consisting of rods of β brass (β -CuZn) coated with the electrolytic layer of pure copper was studied. For the exact fixation of the interface between β brass and copper, a chemically inert thin molybdenum wire was coiled on the β brass rod. After long-term annealing, the molybdenum wire was shifted together with the initial interface towards β brass. The mutual diffusion of Cu and Zn initiates the solid-state reaction



where the α brass layer (α -Cu(Zn)) grew on the β -CuZn/Cu interface and reduced the thickness of the β brass layer. This is possible if the diffusion of zinc to copper exceeds the diffusion of copper to β brass. This effect was interpreted as direct experimental evidence of the vacancy diffusion mechanism rather than the direct exchange of atoms, as was accepted previously [1–3].

The subsequent experimental investigations of the Kirkendall revealed the spatiotemporal instabilities in

the motion of inert markers (Kirkendall planes). Two or more Kirkendall planes are formed in some diffusion pairs [2]. New approaches were proposed to explain the Kirkendall. In particular, the dynamical explanation of the Kirkendall is developed [3].

Since the diffusion of one atom is faster than that of other atoms and the appearing vacancies move in opposite directions and can be grouped together, voids called Kirkendall voids are formed. Although many factors controlling the formation of these voids are not known exactly, the vacancy mechanism is often used to explain the solid-state synthesis of hollow nanostructures [4].

The current explanation of the Kirkendall implies that the diffusion of Zn from the β brass to the Cu layer is primary and the synthesis of the α brass in reaction (1) is secondary. The main aim of this work is to show that the atomic transfer of Zn from the β brass to the copper layer in the Kirkendall experiments is initiated not by the diffusion determined by the difference between the concentrations, but by the long-range chemical interaction between Cu and Zn atoms through the formed α brass layer attributed to solid-state reaction (1).

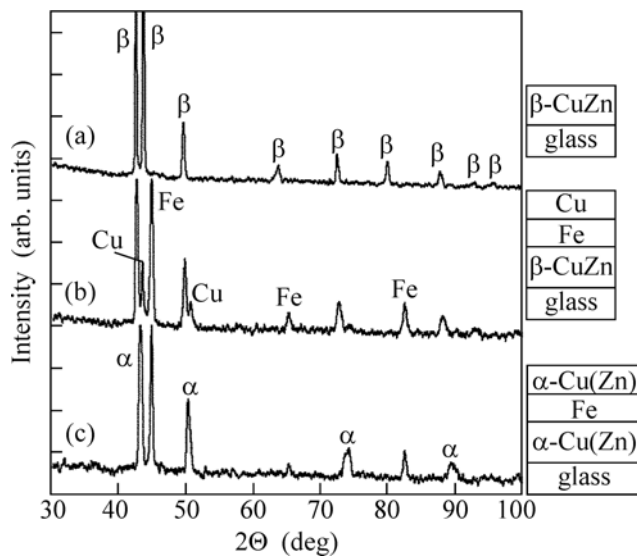


Fig. 1. Diffraction patterns and schemes (a) of the initial β -CuZn film with the composition $\text{Cu}_{60}\text{Zn}_{40}$, (b) after the successive deposition of the 420-nm barrier Fe layer and Cu layer, and (c) after the annealing of the Cu/Fe/ β -CuZn film system at 250°C.

SAMPLES AND THE EXPERIMENTAL PROCEDURE

The experiments were performed with β -CuZn layers with the weight composition $\text{Cu}_{60}\text{Zn}_{40}$ obtained using the solid-state synthesis of bilayer Zn/Cu films deposited on glass substrates in a vacuum of 10^{-6} Torr. The initial Cu/Fe/ β -CuZn samples were manufactured by the successive deposition of Fe and Cu layers onto the preliminarily prepared β -CuZn film. For comparison, we also used the Cu/ β -CuZn samples without any diffusion barrier (a thin-film analog of the Kirkendall experiment). The thicknesses of the Cu and β -CuZn layers were 400–500 and 800–1000 nm, respectively. The thicknesses of the chemically inert Fe barrier layers were 420 and 850 nm. The initial samples were successively annealed in a vacuum of 10^{-6} Torr from 30 to 300°C with a step of 30°C for 60 min at each temperature. The appearing phases were identified using a DRON-4-07 diffractometer ($\text{CuK}\alpha$ radiation). The surface composition was analyzed with an X-ray photoelectron spectrometer (SPECS GmbH). The spectra were recorded under the excitation of the Mg $\text{K}\alpha$ line of the anode of the X-ray tube after the cleaning of the surface by an Ar^+ ion beam (5 kV, 30 μA) for 2 min. The X-ray fluorescence spectrum method was used to determine the chemical composition and thickness of the films. The magnetic moment of the sample was measured using a torque magnetometer in fields up to 18 kOe. The electric resistance was measured by the four-probe method. The measurements were performed at room temperature.

EXPERIMENTAL RESULTS

In the preliminary experiments, it was shown that Cu and Zn do not react with Fe up to a temperature of about 350°C. The magnetization of bilayer Zn/Fe films remains unchanged in this case; the diffraction patterns include only the peaks from Zn and Fe and do not contain reflections from the intermetallic phases. Moreover, the X-ray fluorescence analysis indicated the complete desorption of Zn atoms from the Fe surface at temperatures above 350°C. This is in agreement with the results reported in [5], where the mixing in the diffusion Zn/Fe pairs was observed above 450°C. Copper does not react with iron, because the Fe–Cu system has a positive mixing enthalpy and the mixing on the Cu/Fe interface begins only above 850°C that is the eutectoid decay temperature [6]. An important result of the preliminary experiments is the absence of atomic mixing at the interfaces in the Zn/Fe and Cu/Fe film systems annealed up to 350°C. This fact allows us to use the buffer Fe layer between the Cu and β -CuZn layers to suppress reaction (1).

In the first series of the experiments, the solid-state synthesis of the intermetallic phases of the Zn–Cu system in the bilayer Zn/Cu films was investigated at various annealing temperatures. The diffraction patterns of the initial Zn/Cu samples prepared by depositing the Zn film on the Cu layer contain reflections from the ϵ - CuZn_5 phase even at room temperature for any ratio of the thicknesses. Therefore, the initiation temperature of the ϵ - CuZn_5 phase is below room temperature. Annealing in the temperature range of 110–130°C gives rise to the synthesis of the γ - Cu_5Zn_8 phase in the samples with a Cu content of 45–55 wt %, whereas in the samples with a Cu content of 55–65 wt %, the β -CuZn phase is predominantly formed. The ϵ - CuZn_5 and γ - Cu_5Zn_8 phases were previously observed in galvanic Zn coatings on a Cu substrate aged at room temperature [7]. However, reflections that can be attributed to the α_1 , β_1' , and β_1'' phases appear in the Cu-content range of 55–65 wt % (see Fig. 1a). Consequently, the initiation temperatures of the γ - Cu_5Zn_8 and β -CuZn phases are close or the same. The formed β -CuZn phase is structurally unstable and is partially transformed into the bainite α_1 phase or martensite β_1' and β_1'' phases. A 400- to 500-nm Cu layer, which was sufficient for the formation of α brass, was deposited on the $\text{Cu}_x\text{Zn}_{1-x}$ samples ($x = 45$ –65 wt %). All of the samples annealed at a temperature of 200°C exhibit only the α -Cu(Zn) phase in the products of the reaction. It is important that the γ - Cu_5Zn_8 , β -CuZn, and α -Cu(Zn) phases have different colors; for this reason, their formation is easily observed visually. According to the first series of the experiments, reaction (1) accompanying the Kirkendall has a low initiation temperature below 200°C.

In the second series of the experiments, in order to suppress Kirkendall reaction (1), 420- and 850-nm

inert Fe layers were introduced between the Cu and β -CuZn layers with a weight composition of $\text{Cu}_{60}\text{Zn}_{40}$. The resulting Cu/Fe/ β -CuZn samples (see Fig. 1b) were successively annealed to the initiation of solid-state reaction (1) whose initiation temperature was $T_0 \sim 250^\circ\text{C}$. The initiation temperature was determined from the bend in the temperature dependence of the electric resistance. The reaction at $T_0 \sim 250^\circ\text{C}$ was also easily observed visually, because both sides of the Cu/Fe/ β -CuZn sample acquire a red color characteristic of α brass. The diffraction patterns confirm the formation of α brass on both sides of the barrier Fe layer (see Fig. 1c).

The X-ray photoelectron spectra of the initial Cu/Fe/ β -CuZn films with a 420-nm Fe barrier layer contained only the lines of the upper metallic Cu layer, as well as oxygen and carbon of surface pollutions (see Fig. 2a). After annealing at 250°C , the spectra indicate the appearance of Zn in the upper Cu layer (see Fig. 2b). The spectrum contains the 1021.8-eV Zn $2p_{3/2}$ line and the Zn $L_3M_{4,5}M_{4,5}$ Auger line, which is split into the components with kinetic energies of about 988 and 992 eV belonging to the oxide and metal, respectively. After 50-min ion etching, Zn with the same concentration was observed throughout the depth (~ 100 nm) (see Fig. 2b).

The appearance of Zn in the upper Cu layer in the Cu/Fe/ β -CuZn films with an 850-nm Fe barrier layer was observed after 3-h annealing at 250°C .

The magnetization of the Cu/Fe/ β -CuZn films before and after annealing remained unchanged within the experimental accuracy. Hence, the atomic migration of Zn atoms through the Fe layer does not lead to the formation of intermetallic compounds or a solid solution.

DISCUSSION OF THE RESULTS

The above results certainly indicate that the 420- and 850-nm chemically inert Fe buffer layers do not prevent reaction (1), but slightly increase the initiation temperature. Since Zn atoms in the β -CuZn layer and Cu atoms in the copper layer are spatially separated by the chemically inert Fe barrier, it is reasonable to assume that the chemical interaction between the β -CuZn and Cu layers expands through the 850-nm inert Fe layer, which is four orders of magnitude wider than the length of the usual chemical bond in the metals. The absence of the migration of Cu and Zn in the bilayer Zn/Fe and Cu/Fe films and the intense migration of Zn in the trilayer Cu/Fe/ β -CuZn film system allow us to propose a new view on the nature of the atomic transfer in the Kirkendall. The atomic migration is initiated by the strong long-range chemical interaction, which is associated with the synthesis of the α -Cu(Zn) phase, rather than by the diffusion random walk of Zn atoms, which is due to the difference

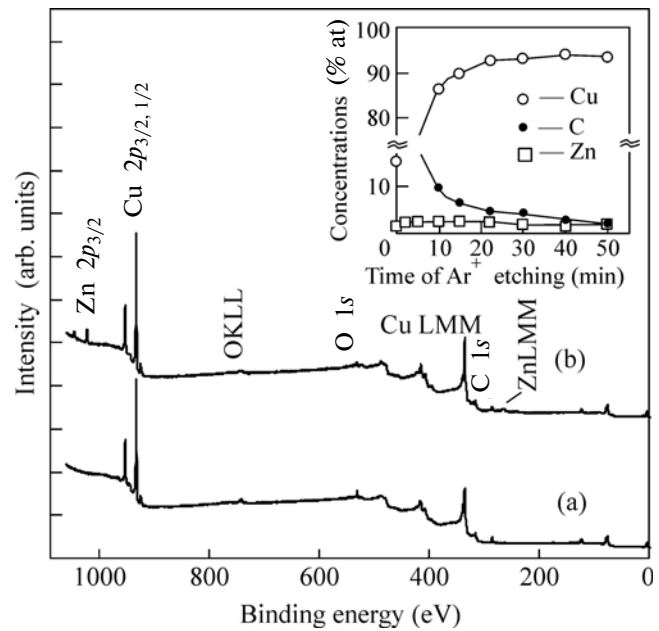


Fig. 2. X-ray photoelectron spectrum of the Cu/Fe/ β -CuZn film system with the 420-nm barrier Fe layer (a) for the initial sample and (b) after annealing at 250°C . The inset shows the concentration profiles in the upper Cu layer.

between the Zn concentrations in the β -CuZn and Cu layers.

It is well known that the Kirkendall was used to investigate diffusion in solids on the basis of the main concepts developed for gases and liquids. However, diffusion mixing in gases and liquids is not accompanied by a reaction. Diffusion in solids often results in the formation of new compounds and solid solutions. The results of this work imply that the atomic transfer in the solid state includes two main processes. The first process is classical diffusion through the grain boundaries and dislocations, which creates an atomic flux in the direction of decreasing concentration. The second process is the directional migration of atoms induced by the strong attractive interaction between reacting atoms (molecules), which breaks old chemical bonds in the initial reagents and creates their directional transfer towards each other through the layer of the reaction product. This migration leads to the formation of a new compound. The diffusion coefficient at low temperatures is very small. The extrapolation of the diffusion coefficient of Zn in Fe from high temperatures to 200°C gives $D_{\text{diffusion}} < 10^{-26} \text{ m}^2/\text{s}$ [8]. According to the above experimental data, the effective diffusion coefficient of Zn through the Fe barrier due to reaction (1) is $D_{\text{reaction}} = d^2/t \sim 10^{-16} \text{ m}^2/\text{s}$; i.e., $D_{\text{diffusion}} \ll D_{\text{reaction}}$. Hence, the atomic transfer induced by reaction (1) dominates over the transfer associated with the diffusion random walk of atoms induced by the concentration gradient.

An unique feature of the solid-state reactions in bilayer thin films and multilayers is the formation of only the first phase at the interface; the formation of this phase begins only above the initiation temperature T_0 . A further increase in the temperature results in the successive formation of other phases (phase sequence) [9]. Any ab initio assumptions regarding the justification of the first phase, phase sequence, and initiation temperatures are absent at present. The reported results indicate that the solid-state reaction between Cu and Zn begins below room temperature with the formation of the first ε -CuZn₅ phase and the phase sequence ends with the α -Cu(Zn) phase having the initiation temperature $T_0 < 200^\circ\text{C}$. Therefore, in order to study the diffusion induced by the concentration gradient, temperature annealings in the Kirkendall should be performed below 200°C . The three Kirkendall experiments were performed at the annealing temperatures of 450, 780, and 785°C , which are much higher than the temperature $T_0(\alpha\text{-Cu(Zn)})$. According to these results, the chemical interaction is the main cause of the migration of Zn atoms from the β -CuZn layer to the Cu layer in the Kirkendall.

Direct electron–electron interactions at interatomic distances provide chemical bonds, which decrease rapidly with an increase in the distance. However, this behavior is inconsistent with the long range of the chemical interaction observed in this work. Nevertheless, the long-range effects have been certainly identified, explained with various justification degrees, and discussed in various fields of the physics of condensed matter. The main of these effects are the directional growth through the amorphous buffer layers [10], the long-range effect of ion implantation on the structure and properties of semiconductor and metallic materials [11, 12], the long-range capillary interactions in liquid films [13], the long-range atomic interactions in the melting of metallic surfaces [14], and the long-range interaction between adsorbates on the metallic surfaces [15]. The experimental investigation and theoretical explanation of the photoassociation-induced formation of purely long-range ultracold molecules constitute a new field of atomic physics [16], where giant helium dimers with nuclei spaced at a distance of $1150\alpha_0$ (where $\alpha_0 \approx 0.053$ nm is the Bohr radius) [17]. For this reason, the long-range effects can underlie the chemical interaction between atoms involved in a reaction.

The long-range chemical interaction was recently revealed in Ni/Ag/Fe [18], Cu/Co/Au [19], and Cd/Fe/Au [20] film systems. The Auger spectroscopy and photoelectron investigations show that predominantly (perhaps only) one kind of atom migrates through the barrier layer in all of these systems. An analysis indicates that these atoms are atoms of metals having a low melting temperature. The dominant migration of only one kind of atom in the solid-state reaction was observed in many investigations [21].

These data are in agreement with the reported experimental results, where the migration of Zn atoms through the inert Fe buffer layer to the upper copper layer is observed, and with the main conclusion of the Kirkendall experiments that the diffusion of Zn atoms to the Cu layer is faster than the diffusion of Cu atoms to β brass.

CONCLUSIONS

The solid-state reaction of copper with β brass with Cu/ β -CuZn and Cu/Fe/ β -CuZn film systems with the inert Fe barrier layer, which is responsible for the Kirkendall, has been investigated by X-ray diffraction, photoelectron spectroscopy, and magnetic structure measurements. The formation of α brass at any thickness of the Fe barrier certainly indicates that the migration of Zn atoms from β brass to the Cu layer is initiated by the strong long-range chemical interaction, which is associated with the synthesis of α -Cu(Zn) phase, rather than by the diffusion flow induced by the concentration gradient, as is commonly accepted at present. The reported data and analysis of the solid-state reactions in the presence of diffusion barriers make it possible to arrive at an unprecedented conclusion that the long-range chemical interaction plays a decisive role in the atomic migration accompanying low-temperature SP transformations and reactions.

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