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Interfaces between Pb grains and Cu surfaces

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Abstract The interfaces between liquid or solid Pb islands and single- or poly-crystalline Cu substrates are investigated. EBSD (Electron backscattered diffraction) analyses show that when Pb is solidified from droplets, a cube-on-cube orientation relationship prevails between the Pb crystals and each Cu grain surface, whatever its surface orientation, even though the lattice parameter of Pb is 1.37 times larger than that of Cu. Scanning electron microscope (SEM) and atomic force microscope (AFM) analyses show that during annealing of Pb droplets, ridges develop at the droplet-substrate triple lines, indicating that the interfaces evolve towards equilibrium by diffusional processes. These features are discussed in comparison with experiments and calculations performed on Pb nanocrystals embedded in Al, another fcc solid with a lattice parameter smaller than that of Pb. It is proposed that the cube-on-cube orientation relationship results from the solidification of Pb along the {111} planes of the solid Cu/liquid Pb interface which have developed by diffusion during the process of equilibration of the interface shape.

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Introduction

Micron-sized droplets of Pb solidify as single-crystals on different solid substrates, such as graphite, vitreous carbon, or copper, with which Pb has negligible mutual solubility [1–3]. When the Pb crystals are annealed a few degrees below the melting point of Pb, they evolve towards their equilibrium shape, and {111} and {100} facets develop at the surface of the crystal [1]. Thus, the epitaxial relationship between Pb crystals and substrates of different orientations can be partially identified from the location of the Pb crystal facets in relation to the substrate. It has been observed, for example, that the {111} and {100} planes of Pb crystals solidified from drops lie parallel to surfaces of {111} and {100} Cu substrates, respectively [3], and that the {111} planes of solidified Pb drops are parallel to the graphite basal plane [1, 4]. The same type of epitaxy was observed for Pb on Si [5]. In this paper we present the results of a study on the orientation relationship (OR) between Pb crystals solidified on different {hkl} surfaces of Cu. We find that a cube-on-cube OR prevails, which is surprising given that the ratio of lattice parameters: a_{Pb}/a_{Cu} is 1.37. We propose that the shape of the interface (or contact area) between Pb and Cu, formed during the time that Pb was liquid, is probably at the origin of the observed OR. Our proposition will be supported by experiments and calculations performed in the Pb/Al system.

Experiments

A 200 μm thick polycrystalline Cu substrate was prepared from 99.999% pure Cu cold-rolled by 50%

reduction. The sample was polished with diamond paste down to 100 nm, then mechano-chemically polished with 200 nm colloidal silica in a basic solution, which slightly dissolves the cold-rolled surface of Cu. After polishing, the sample was annealed at 1223 K under an Ar-10%H_2 flux for 250 h. During annealing, the copper recrystallizes and O and S are removed from the sample. O and S are known to adsorb and cause microfaceting of the Cu surfaces. Examination of the annealed sample by SEM showed that it was free of any microfacets.

Pb was deposited on the Cu substrate in a UHV chamber at a pressure in the 10^{-8} Pa range. Before deposition, Cu was heated up to 973 K in order to remove any physisorbed species. A layer of 99.9999% pure Pb, about 1 μm thick, was then deposited on the Cu surface by PVD. After deposition, the sample was transferred to a scanning Auger microscope. The surface was sputtered with Ar until the Auger spectrum displayed only Pb. Then the temperature was increased up to the melting point of Pb where the Pb film broke up into droplets. Their sizes ranged between 500 nm and 20 μm. The droplets were randomly distributed on the grains of the polycrystalline Cu substrate, with some of them straddling grain boundaries. During the experiment, the Pb droplets were liquid for about 8 h. After cooling, the droplets solidified into single-crystals, whether they were located within grains or straddling the grain boundaries. Then the sample was annealed for 15 h at about 580 K. Under these conditions, {111} and {100} facets develop on the surface of the Pb crystals [1].

The sample was ‘‘quenched’’ to room temperature by turning off the heating, and examined in a field emission gun scanning electron microscope (FEG-SEM) (Jeol 6320F—cold cathode) equipped with capabilities for electron backscattered diffraction (EBSD) using a low light level digital camera and the Channel 5 system from ‘‘HKL technology’’. The sample was also examined in an atomic force microscope (AFM) from PSIA, which was used to acquire information on the 3D shape of the Cu surface and the Pb crystals.

A second sample was prepared using a Cu(100) single crystal substrate. This sample was examined by AFM in regions where the Pb deposit was thin, and produced small droplets which evaporated during annealing 30 K above the melting point of Pb.

Results

Surface features

Figure 1 displays two versions of an AFM photomicrograph which illustrates several features that occurred during annealing of the pure copper polycrystal at 1223 K, and the subsequent heating of the polycrystalline copper substrate with its Pb deposit, both above and below the melting point of Pb.

(1) The grain boundaries at the copper substrate surface underwent grooving during annealing of the Cu polycrystal at 1223 K under hydrogen.
(2) The Pb particles consist of single-crystals in the shape of a truncated sphere, and display a large facet (probably of (111) orientation [1]). This facet belongs to the equilibrium crystal shape (ECS) of a Pb crystal close to its melting point. However, the size of the crystals is too large for these facets to have fully reached their equilibrium size.
(3) Copper ridges are formed at the foot of the drop where the surface of the Pb crystal is connected to the Cu substrate. This ridging results from the local shape equilibration of the drop-substrate system under the influence of interfacial energies (namely: the surface energy of the solid substrate, the surface energy of the particle, and the interfacial energy between the particle and the substrate) [6, 7]. This phenomenon will be discussed in more detail later.

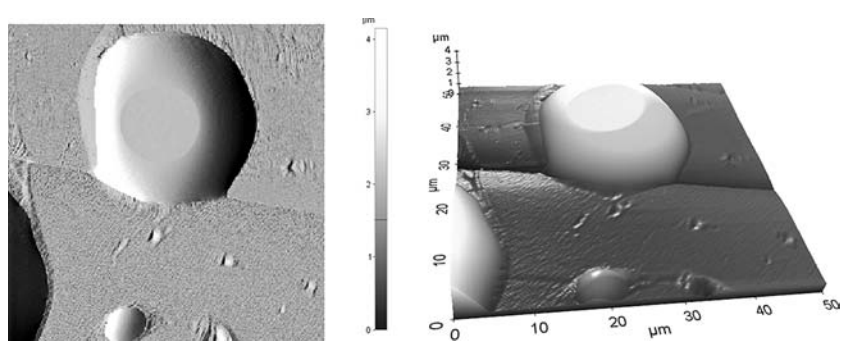

Fig. 1 AFM picture of a Pb crystal close to a grain boundary of Cu

Figure 2 displays AFM and scanning electron microscopy (SEM) micrographs of the foot of a drop, and shows that the surfaces of the Cu substrate and the ridge are micro-faceted. This microfaceting may be induced during annealing of the sample above and below the melting point of Pb. At these temperatures, Pb diffuses from the crystal or drop and adsorbs on the Cu surface [8, 9]. The adsorbed Pb may significantly increase the diffusivity of Cu over the surface [10], thereby producing a microfacetting of the Cu surface, as is known to occur when Bi is adsorbed on Cu [11]. Pb could also enhance the Cu surface energy anisotropy, as Bi is known to do [12], thereby leading to a fully faceted equilibrium crystal shape.

Orientation relationship

Figure 3 shows two SEM pictures of Pb crystals distributed on several grains and at GB's. As the sample was contaminated during storage under a poor vacuum in a desiccator, the quality of the image is poor. The crystals are not simple truncated Wulff shapes because of constraints on their shapes imposed by the ridging. However, it can clearly be seen that the Pb crystals on one grain are all in the same orientation relationship to the substrate (fiber texture). This can be detected by looking at the large facets on the crystals. The Pb crystals straddling the GB are also single-crystals and their orientation is parallel to that of the Pb crystals on one of the two grains.

The sample was analyzed by EBSD in order to investigate the orientation relationship between the Pb crystals and Cu substrate grains of random orientation. Figure 4a shows a low resolution SEM image of the region of the sample analyzed by EBSD. The conditions of observation are optimized for the electron back scattered patterns (EBSP) contrast, but not for the secondary electron imaging. (i.e. a high probe current of 1 nA and a long working distance of 25 mm, which prevents imaging in the high resolution mode).

In Fig. 4, the sample is tilted by 70° from the horizontal, in order to improve the quality of the EBSP [13]. At lower angles, the energy of the electrons is scattered and the EBSP becomes blurred. Under these conditions, Pb crystals which make a contact angle greater than 20° will be imaged only partially. This is the case for the larger Pb crystals, for which the contact angle is about 40°. Because of ridging, and a shape that is probably closer to the ECS, the smaller crystals are entirely seen. Consequently just a part of the larger Pb crystals can produce clear and contrasted Kikuchi line patterns suitable for reliable automated analysis of the surface orientation. Figure 4b shows a colored EBSP map of the sample where the non-analyzable points are left in white. Figure 4c gives the surface orientation of the copper grains. Figure 5 is a schematic which

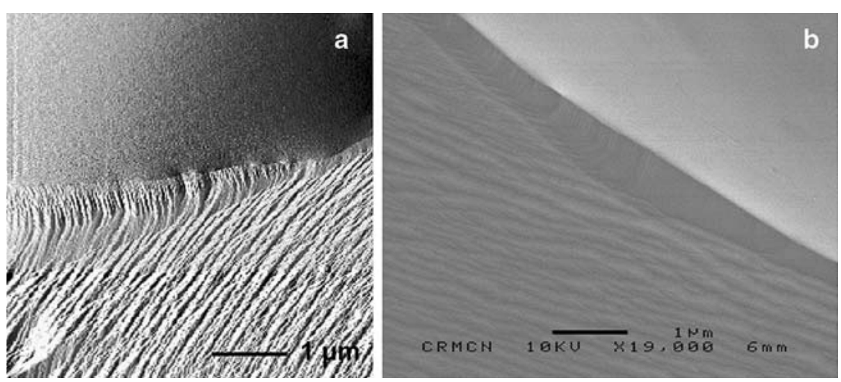

Fig. 2 (**a**) AFM and (**b**) SEM pictures of the foot of a Pb crystal. The contrast on the SEM picture, shows that the ridge is made of copper. The bar scale of the SEM picture also stands for the AFM picture

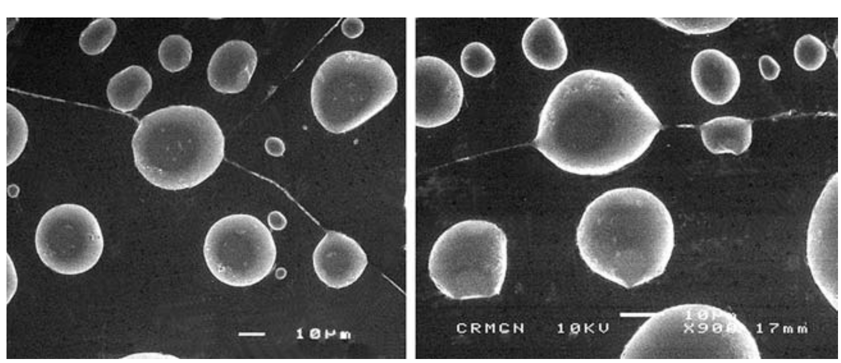

Fig. 3 SEM images showing Pb crystals solidified on Cu grains

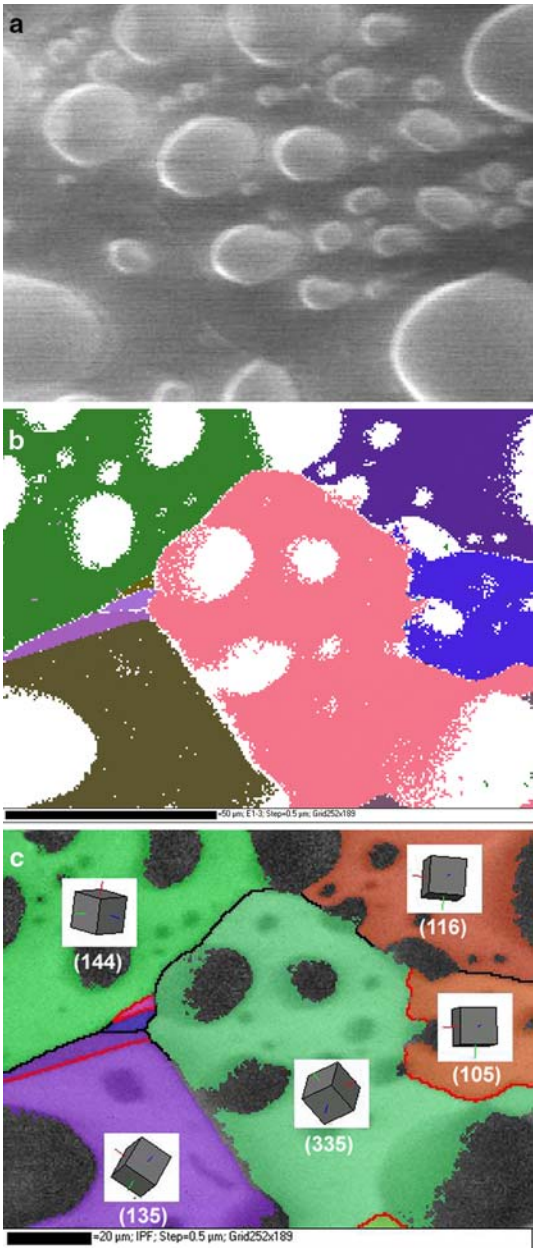

Fig. 4 (**a**) Secondary electron image of Pb crystals on Cu grains of different surface orientations. (**b**) Orientation map of the same region. The color of one pixel corresponds to a set of the 3 Euler angles fully describing the cristallographic orientation of the piece of surface corresponding to that pixel. The white pixels which were not indexed belong to Pb crystals. Comparing the two pictures, the pixels of the Pb crystals which have been indexed have rigourously the same color as the Cu grain on which they lie. This means that the Pb crystal are in cube-on-cube epitaxy on the Cu grains whatever their surface orientation. (**c**) orientation of the surface of the copper grains

describes the region of a spherical cap that can produce contrasted and indexable EBSP, as a function of the contact angle of the spherical cap on the surface (assuming that an EBSP is indexable if the angle between the surface and the horizontal is roughly between 55 and 85°).

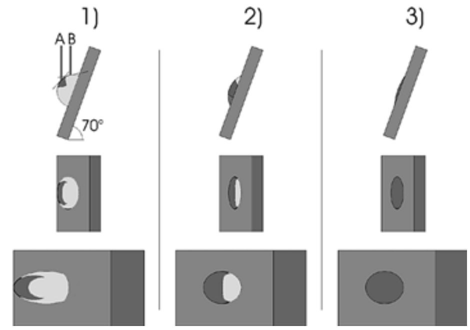

Fig. 5 Sketchs of analyzed zone of the drop (named A, and in dark) as a function of the contact angle of the crystal on the substrate and corresponding to images in projection (second line) and in projection with a tilt correction (third line) (1) for a contact angle of 90°; (2) for a contact angle of 45°; (3) for a contact angle less than 20°

In Fig. 4b, the color of the pixels is related to the three Euler angles that describe the sample surface orientation relative to the crystal. The software analyzes the Kikuchi bands at each point on the sample surface, and determines the orientation and whether it belongs to the Pb or the Cu crystal. The two materials have a fcc structure, but the lattice parameter is 1.37 times larger for Pb; consequently, the width of the Kikuchi bands are narrower for Pb (see Fig. 6). The quality of the Kikuchi patterns allows a determination of the orientation to within ±1°. Figure 4b clearly shows that the set of Euler angles are identical for Pb crystals that lie on a given Cu grain of the substrate. This is evidence of a cube-on-cube OR of the Pb on the Cu. Any Pb crystal sitting on an emerging GB adopts the orientation of one of the two adjacent grains.

Ridging and solid/liquid interface shape

Pb droplets on a Cu(100) were annealed for 8 h under UHV at 610 K (10 K above the melting point of Pb). After this treatment, the temperature was raised to 640 K, leading to the evaporation of the smallest (micron-sized) Pb droplets. Figure 7 displays two AFM and one SEM micrographs of the Cu(100) surface after (total or partial) evaporation of the smallest Pb droplets. At the location of each ex-droplets, the Cu ridge, which was visible at the foot of the drops before their evaporation (Fig. 2), is observed to have grown by diffusion of the copper atoms from the solid/liquid interface. At the location marked by an arrow in Fig. 7a, a drop has formed two ridges before its complete evaporation. A topography profile along the section marked by a line is shown on the right side of

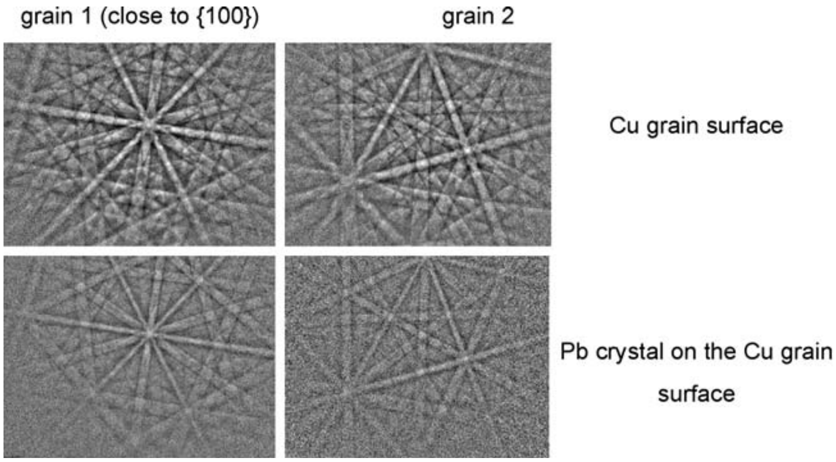

Fig. 6 Kikuchi patterns of Cu (top) and Pb (bottom); two series of a Pb crystal and the Cu grain on which it is sitting. Both components are fcc, but the EBSP of Pb shows narrower Kikuchi bands than those for Cu because Pb has a larger lattice parameter than Cu

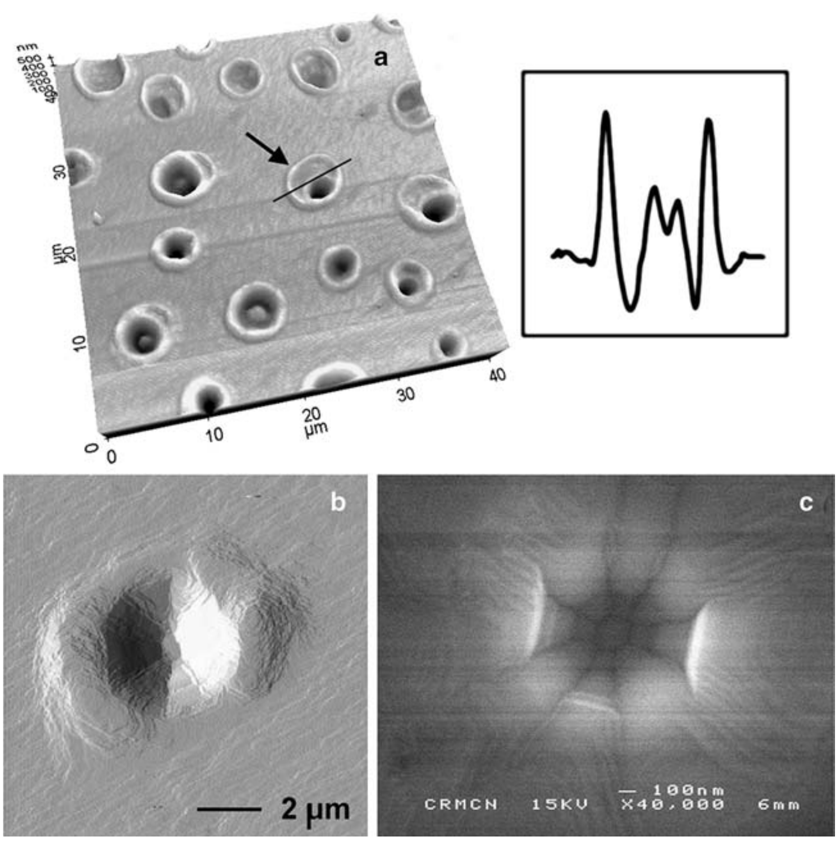

Fig. 7 (**a**) AFM picture of the ex-interfaces between Cu (100) and Pb; (**b**) AFM picture of one feature (**c**) SEM picture of the same type of feature

Fig. 7a. At its initial location, a first ridge was formed. Then, because of its volume decrease by evaporation, the drop receded inwardly away from the first ridge. At this location, a new ridge was formed before evaporation was completed. The smaller drops shown in this image display a single ridge. Between the two ridges of the arrowed feature, the interface is flat and its level is below that of the copper surface. The topography profile clearly shows that the surface between the two ridges is depressed. Thus the copper atoms forming the ridge were removed from the whole solid/liquid interface. This suggests that the ridge formed by dissolution/precipitation (i.e. diffusion through the liquid) rather than by interface diffusion of the copper atoms along the solid/liquid interface. Figures 7b, c detail the shape of the prior solid/liquid interface beneath a small drop which has formed a single ridge. The shape given by AFM is distorted by a convolution with the shape of the AFM tip. However, the SEM picture shows that the hole has a conic dissolution shape with stepped facets displaying four-fold symmetry. The facets include probably low index planes such as {111}.

Discussion

The epitaxy of micron-sized Pb crystals on low index copper surfaces, e.g. (111) and (100), has already been observed. The tops of the Pb crystals on these surfaces display (111) or (100) facets, which are parallel to the respective substrates [3]. However, those experiments were not able to determine the complete OR of solid Pb on Cu. The present experiment can also determine the rotation angle of the two lattices with respect to each other. The cube-on-cube OR is surprising, because it does not minimize the misfit between the two lattices, as is known to occur in other systems (e.g. the Kurdjumov–Sachs OR between fcc and bcc phases of ferrite/austenite interfaces). Also, it is usually found that fcc metal grains prepared by physical vapor deposition are textured, with {111} planes tending to lie parallel to the substrate, for many different substrates. This is related to minimization of surface energy [14]. We actually observed this {111} fiber texture for Pb deposited on Cu (100).

Interestingly, a similar cube-on-cube OR has also been observed for nanometer-sized Pb particles fully embedded in Al [15]. Al crystallizes in the fcc structure but has a lattice parameter that is 1.27 times smaller than that of Pb. The solid Pb particles are fully faceted, and are completely bounded by {111} and {100} planes. After melting, the liquid Pb inclusions still display facets along the {111} orientations of Al [16]. The atomistic simulations of Shi et al. [17] on the same system qualitatively reproduce the shape of a melted Pb particle in Al in that the solid/liquid interface displays only {111} facets. Another interesting point of the simulation is that the Pb atoms in the liquid phase are ordered along these {111} facets. Thus, we suggest that the local order, which prevails in the liquid along {111} Al facets, may facilitate the adoption of cube-on-cube OR upon subsequent solidification. The origin of the cube-on-cube OR between small Pb crystals and any Cu{hkl} surface can thus be explained by combining this suggestion with the fact that the solid Cu/liquid Pb interface is reshaped during ridge formation thereby developing {111} facets.

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