

# Orientation relationships of copper crystals on sapphire (1 0 $\bar{1}$ 0) m-plane and (1 0 $\bar{1}$ 2) r-plane substrates



Dominique Chatain<sup>a,\*</sup>, Stefano Curiotto<sup>a</sup>, Paul Wynblatt<sup>b</sup>, Hila Meltzman<sup>c</sup>, Wayne D. Kaplan<sup>c</sup>, Gregory S Rohrer<sup>b</sup>

<sup>a</sup> Aix-Marseille Université, CNRS, CINaM UMR 7325, 13288 Marseille, France

<sup>b</sup> Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

<sup>c</sup> Department of Materials Science and Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel

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## ABSTRACT

Copper films deposited on m- and r-plane sapphire substrates have been dewetted in either the solid or the liquid state, and equilibrated at 1253 K. The orientation relationships (ORs) between the dewetted copper crystals and the sapphire substrates have been investigated by electron backscatter diffraction. In addition, the shape of the copper/sapphire interface has been studied by scanning electron microscopy. Although the as-deposited films develop {1 1 1} surfaces parallel to both substrates, after solid state dewetting the copper crystals on the m-plane substrate are found to change their interface plane from Cu{1 1 1}||Al<sub>2</sub>O<sub>3</sub>(m-plane) to Cu{1 1 1}||Al<sub>2</sub>O<sub>3</sub>(a-plane), and after liquid state dewetting the preferred OR of copper on both m- and r-plane substrates may be expressed as: Cu{1 1 1}⟨1 1 0⟩ || Al<sub>2</sub>O<sub>3</sub> {1 1  $\bar{2}$  0} ⟨0 0 0 1⟩. This OR is identical to that previously observed for copper on the sapphire a-plane.

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## 1. Introduction

There has been considerable recent interest in metal/metal–oxide interfaces in applications such as electronic devices and metal–ceramic joining. The structure and properties of these interfaces depend in large part on the crystallographic orientation of the metal–oxide substrate, as the orientation relationships (ORs) that develop between the metal and the substrate may vary from one substrate orientation to another. The goal of both our present and previous studies on this topic [1,2] has been to develop better understanding of the factors that control the ORs of fcc metals on sapphire, using copper/sapphire as an example. This is a particularly convenient model system because the copper surface energy is almost isotropic (the maximum surface energy anisotropy is only ~1%) so that the minimum energy ORs will be dictated primarily by the anisotropy of the sapphire/copper interfacial energy.

The experimental approaches we have adopted have been different from those of other studies. We have equilibrated copper deposits by two different techniques: either by solid state or by liquid state dewetting. As discussed in more detail below, liquid

state dewetting is more likely to produce equilibrium ORs. In addition, the crystallographic details of the OR have been determined by electron backscatter diffraction (EBSD). This allows measurements to be performed on many tens, or even hundreds of copper particles, and thus produces more reliable statistics on the preferred OR than methods such as high-resolution transmission electron microscopy (HRTEM), where the number of possible measurements is necessarily much more limited.

The ORs that develop in the copper/sapphire system have been the subject of many previous investigations. These have focused primarily on (0 0 0 1) sapphire (c-plane) substrates [1,3–8]. In that case, our studies have found that the observed ORs are strongly dependent on the method of sample preparation, and have demonstrated that multiple ORs are observed because they all possess approximately the same copper/sapphire interfacial energy [1]. We have also previously studied the OR of copper on the (1 1  $\bar{2}$  0) sapphire a-plane [2]; this substrate has also been the subject of a couple of other studies, both performed by HRTEM [9,10]. For this substrate orientation, our studies have concluded that the most frequent OR is Cu(1 1 1) || Al<sub>2</sub>O<sub>3</sub>(1 1  $\bar{2}$  0) and Cu(1 1 0) within few degrees from Al<sub>2</sub>O<sub>3</sub>[0 0 0 1]. Although Sasaki et al. [10] also observed the same OR, it was identified as a low frequency OR; however, the HRTEM technique used in their study does allow reliable statistical analysis. Recently, Atiya et al. [11] studied the initial stages of dewetting of a Pt film from a sapphire a-plane

\* Corresponding author.

E-mail address: [chatain@cinam.univ-mrs.fr](mailto:chatain@cinam.univ-mrs.fr) (D. Chatain).

substrate, and analyzed several tens of equilibrated grains by EBSD. They identified 4 different ORs, among which one is identical to the preferred OR found for copper on the same (11 $\bar{2}$ 0) plane of sapphire [2]. However, even with their fairly large sample size, they were unable to identify the preferred OR.

The present paper reports on the preferred ORs of copper crystals grown on sapphire substrates terminated by either the (10 $\bar{1}$ 0) or the (10 $\bar{1}$ 2) plane (also referred to as the m-plane or r-plane, respectively). Of the substrate orientations studied thus far, the m-plane of sapphire is the only one that does not appear on the equilibrium crystal shape of sapphire [12,13]. This surface of sapphire is known to decompose into micro-facets of the r-plane (10 $\bar{1}$ 2) and the s-plane (1 $\bar{1}$ 01), running along the  $\langle 11\bar{2}0 \rangle$  direction, when annealed under oxygen in the temperature range from 1253 K to 1673 K [14–16]. To our knowledge, there are no data available on the ORs of copper on either the m-plane or the r-plane of sapphire. However, the OR of gold, another fcc metal, on the m-plane, has been investigated by Sadan and Kaplan [16]. After equilibration of gold crystals formed by dewetting a film in the solid state at 1273 K, those authors found that both the surface of sapphire and its interface with gold undergo micro-faceting, with different crystallographic planes for the micro-facets at the surface and at the interface. The sapphire side of the interface consists of (01 $\bar{1}$ 1), (01 $\bar{1}$ 1) and (11 $\bar{2}$ 0) facets, and the preferred OR is Au(111)[1 $\bar{1}$ 0]||Al<sub>2</sub>O<sub>3</sub>(01 $\bar{1}$ )[0001].

## 2. Experimental procedures

Samples were prepared by dewetting copper films deposited on single crystal sapphire substrates. Most of the procedures have been described in a previous paper, in which the ORs of copper on c-sapphire substrates [1] were reported. They are summarized below.

The sapphire substrates used to prepare the samples consisted of single-side epi-polished wafers, 5.08 cm in diameter, purchased either from Gavish<sup>1</sup> or from CrysTec<sup>2</sup>. The m-plane substrates from Gavish had a maximum miscut of 0.1°, and the following maximum impurity concentrations: Mg (20 ppm), Si (15 ppm), Na (10 ppm), Ca (7 ppm) and K (0.5 ppm). One m-substrate purchased at CrysTec was also investigated. The impurity content of the CrysTec sapphire wafer is lower than in the Gavish samples; it contains the same components as those listed above, but at a level of less than 5 ppm. The r-plane substrates were acquired from CrysTec. After ultrasonic cleaning in ethanol for a few minutes, the surface chemistry of the wafers was investigated by Auger electron spectroscopy (AES), and found to consist of Al and O species with traces of C contamination.

Prior to copper deposition, the sapphire substrates were annealed for several tens of hours at 1253 K under an Ar–20%O<sub>2</sub> atmosphere in a furnace fitted with a sapphire tube as described in [15]. After annealing and cooling to room temperature, the sapphire surfaces were re-analyzed by AES to identify any species which may have segregated to the surface, or that may have deposited on the surfaces from the environment during annealing. Traces of K and Mo were detected on all the annealed samples. Some carbon contamination was acquired during sample transfer through air. A comparison of the experiments performed on annealed and as-received substrates shows that the impurities detected at the surface of the sapphire after annealing do not play a detectable role either in the OR, or in the morphology of the interface.

The surface morphologies of the m-sapphire and the r-sapphire were investigated by atomic force microscopy (AFM) using a Park model XE-100 instrument. Fig. 1 shows the sample surfaces after annealing. The m-surface displays micro-facets and the r-surface has

large terraces and steps. The morphology of the cleanest substrates remains similar to that of the as-received samples [15]. The orientations of the facets on the m-plane were confirmed using high-resolution transmission electron microscopy (HRTEM) (see Fig. 1c) from a cross-section prepared using focused ion beam (FIB) milling. They are the r- and s-facets, identified by previous authors [14,16] on the m-substrates annealed in air at 1673 K and 1273 K, respectively.

Copper films were deposited on the sapphire substrates by physical vapor deposition (PVD) in an ultra high vacuum (UHV) chamber fitted with capabilities for AES analysis. The film surfaces were analyzed by AES, and traces of S and Cl were detected. These species were removed during the subsequent annealing of the film under Ar–H<sub>2</sub> [17]. The film thickness ranged from 30 to 180 nm, as measured by AFM.

Copper crystals were formed by dewetting the copper films under an Ar–20%H<sub>2</sub> atmosphere in the sapphire furnace. During experimental runs, the oxygen partial pressure, p(O<sub>2</sub>), of the flowing gas was measured downstream from the sample at about 10<sup>–21</sup> atm by means of an external electrochemical oxygen sensor, as described in [18]. After a stable p(O<sub>2</sub>) was established, the copper films were dewetted either in the solid state at 1253 K or in the liquid state. The diameter of the resulting copper particles ranged from 200 nm to 1 μm. Samples dewetted in the solid state were annealed at a temperature of 1253 K for 78 h. In the case of liquid state dewetting, the temperature was set slightly above the copper melting point (1357 K) for 5 min. The samples were then cooled to 1000 K over a period of 40 min to overcome possible undercooling of the liquid and solidify the droplets. Then, the temperature was reset to the annealing temperature of 1253 K for several hours for equilibration of the copper-sapphire interface without excessive evaporation of the copper particles.

The samples were observed by scanning electron microscopy (SEM, Jeol, JSM-6320F). A carbon film was deposited on one half of the sample surfaces, to avoid charging and facilitate imaging of the copper crystals. On the other half, which was left bare, it was possible to image certain details of the morphology of the sapphire substrate at 3 kV.

The orientation relationships (OR) between the Cu crystals and the sapphire were investigated by automated electron backscatter diffraction (EBSD) mapping in a FEI Quanta 200 FE ESEM equipped with an EDAX/TSL orientation system and the Hikara high speed EBSD detector to record the orientations of Cu and sapphire. Data were acquired at 30 kV at a sample tilt of 70° with respect to the substrate plane. Several carbon-coated areas containing copper particles were scanned in steps of 50 nm, and these were generally merged into a single data set for the purpose of determining the relative frequencies of occurrence of the various ORs. This procedure is described in detail in [1].

The interface morphology between the copper grains and the substrate was investigated by SEM at locations where the copper crystals had been removed either by natural evaporation or by etching with nitric acid. In addition, some samples were prepared by FIB sectioning for TEM observation, in order to check the surface of the m-plane at the atomic scale. Data were acquired in a monochromated and aberration corrected field emission gun TEM (FEI Titan 80-300S/TEM), operated at 300 kV. Kikuchi electron diffraction was used to align the sample in a low-index zone axis, with surface facets parallel to the viewing direction. The results obtained by this procedure have been presented in Fig. 1c.

## 3. Results and discussion

### 3.1. OR of Cu on m-plane sapphire dewetted in the liquid or the solid states

X-ray diffraction (XRD) analysis of the as-deposited polycrystalline copper films on the m-plane substrates has shown that the

<sup>1</sup> Gavish Industrial Technologies & Materials (Omer, Israel).

<sup>2</sup> CrysTec GmbH Kristalltechnologie (Berlin, Germany).

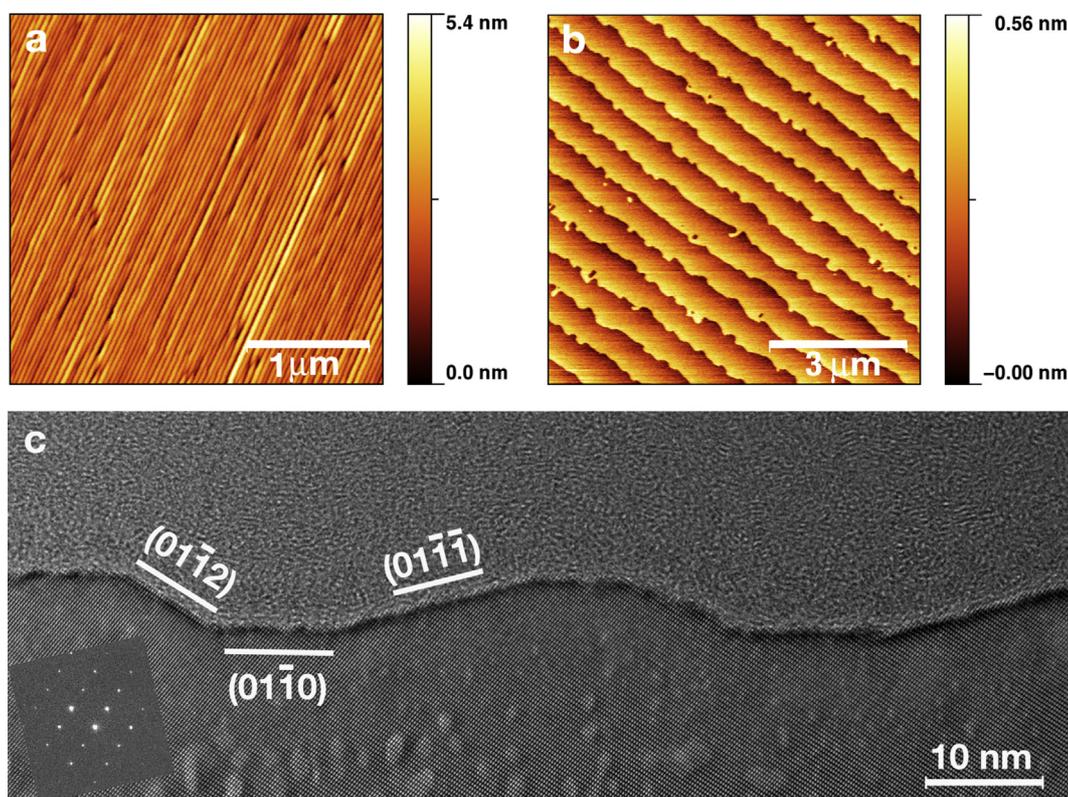
copper grains have one of their  $\{111\}$  planes parallel to the substrate.

Fig. 2a and b present inverse pole figures in the  $[001]$  direction of the microscope reference frame ( $(001)$  IPF), obtained from samples dewetted in the liquid and solid states, respectively, which show the distribution of the planes of the copper particles that lie parallel to the  $m$ -plane sapphire substrate. The figures have been constructed using the OIM-TSL software based on the measured orientations of 865 copper particles from the sample dewetted in the liquid state, and of 188 copper particles from the sample dewetted in the solid state. In order to eliminate any effects that might be due to the size of the copper crystals, only one point per copper crystal has been counted in this statistical analysis.

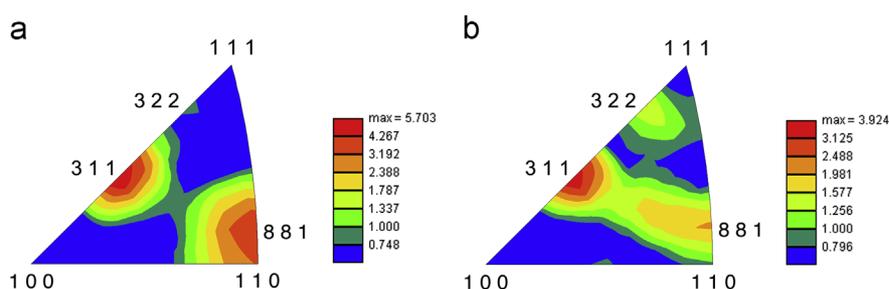
In the case of the sample dewetted in the liquid state (Fig. 2a), the copper particles are divided almost equally between two populations of crystals with their  $\{311\}$  and  $\{881\}$  planes approximately parallel to the  $m$ -plane. In the case of dewetting in the solid state (Fig. 2b), the number of copper particles involved in the statistics is

low. However, it can be seen that the highest-frequency interface plane of the copper particles is  $\{311\}$ . There is also a fairly high frequency of copper particles with  $\{881\}$  planes approximately parallel to the  $m$ -plane. In addition there is a broad band connecting the  $\{311\}$  and  $\{881\}$  poles, which is populated above the background level. This band indicates that there are many crystals with normals inclined at  $\sim 30^\circ$  to  $[111]$ . Lastly, there is also a low frequency of copper particles with an interface plane in the vicinity of  $\{322\}$ , which was not observed in the case of liquid state dewetted samples. These copper crystals are just twins of the  $\{311\}$  Cu crystals.

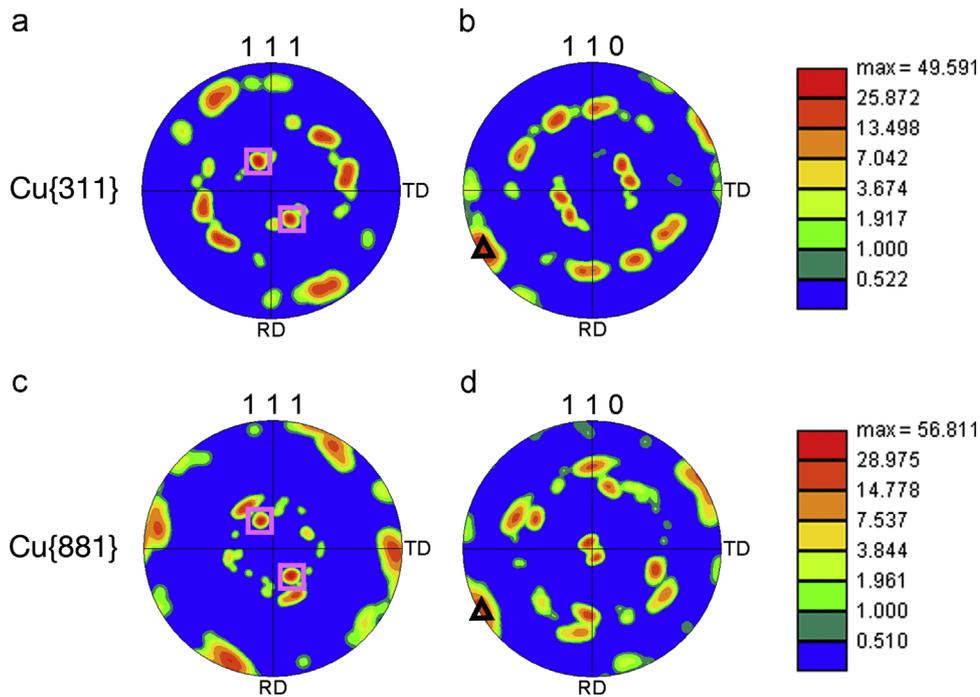
For the sake of clarity, we only provide complete details of the OR obtained on the sample dewetted in the liquid state. For this it is useful to consider Fig. 3, which shows the respective  $\{111\}$  and  $\{110\}$  pole figures (PFs) of the Cu crystals with  $\{311\}$  and  $\{881\}$  planes parallel to the substrate. The pink open squares and the black open triangles in these figures represent poles of the sapphire  $(11\bar{2}0)$  and  $(0001)$  planes superimposed on the Cu  $\{111\}$  and Cu $\{110\}$  PFs of Fig. 3a and c, and of Fig. 3b and d,



**Fig. 1.** Surface morphology of  $m$ - and  $r$ -plane of sapphire after annealing under Ar–20% O<sub>2</sub>. (a) AFM micrograph of the  $m$ -plane substrate. The needles in (a) consist of  $r$ - and  $s$ -plane micro-facets aligned parallel to the  $[11\bar{2}0]$  direction; (b) AFM micrograph of the terraces of the  $r$ -plane substrate; (c) HRTEM of a FIB cross-section of an annealed  $m$ -sapphire substrate viewed along the  $[11\bar{2}0]$  direction where the surface facets are identified.



**Fig. 2.**  $(001)$  IPF of copper crystals dewetted from the sapphire  $m$ -plane (a) in the liquid state, and (b) in the solid state.



**Fig. 3.** (a) and (b)  $\{111\}$  and  $\{110\}$  PFs of copper crystals with a  $\{311\}$  plane parallel to the substrate, dewetted in the liquid state on the m-plane of sapphire; (c) and (d),  $\{111\}$  and  $\{110\}$  PFs of copper crystals with a  $\{881\}$  plane parallel to the substrate, dewetted in the liquid state on the m-plane of sapphire. On these figures the  $\{11\bar{2}0\}$  (pink open squares) and  $(0001)$  (black triangles) poles of sapphire are also plotted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

respectively. The  $\text{Cu}\{111\}$  and  $\text{Cu}\{110\}$  PFs show that there are two variants of the  $\text{Cu}\{311\}$  crystals and two variants of the  $\text{Cu}\{881\}$  crystals. Each of these variants has one  $\text{Cu}\langle 111 \rangle$  direction parallel to one  $(11\bar{2}0)$  sapphire pole (Fig. 3a and c). These sapphire poles do not lie in the plane of the interface since they appear within the PFs, rather than on the outer perimeter of the PFs. Both variants of the  $\text{Cu}\{311\}$  and  $\text{Cu}\{881\}$  crystals also have in-plane  $\text{Cu}\langle 110 \rangle$  directions that lie within  $\sim \pm 3^\circ$  from the sapphire  $(0001)$  pole (Fig. 3b and d). Thus the ORs of both populations of Cu crystals are identical and can be written as:  $\text{Cu}\{111\}\parallel\text{Al}_2\text{O}_3(11\bar{2}0)$  and  $\text{Cu}\langle 110 \rangle$  within few degrees from  $\text{Al}_2\text{O}_3(0001)$ \*. This OR is identical to the OR observed previously in our study of copper on the sapphire a-plane [2]. It is worth emphasizing that even though the IPF of Fig. 2a might suggest the existence of two ORs, each based on a different copper interface plane (i.e.  $\text{Cu}\{311\}\parallel\text{Al}_2\text{O}_3(10\bar{1}0)$ , and  $\text{Cu}\{881\}\parallel\text{Al}_2\text{O}_3(10\bar{1}0)$ , with  $\text{Cu}\langle 110 \rangle$  within a few degrees of  $\text{Al}_2\text{O}_3(0001)$ ), both of these apparent ORs can be described by the single OR given above:  $\text{Cu}\{111\}\langle 110 \rangle\parallel\text{Al}_2\text{O}_3(11\bar{2}0)[0001]$ .

For the case of the sample dewetted in the solid state, the copper crystals display orientations which belong to the broad band connecting the  $\{311\}$  and  $\{881\}$  poles in the  $(001)$  IPF of Fig. 2b. These crystals have a single  $\text{Cu}\langle 111 \rangle$  direction parallel to a  $(11\bar{2}0)$  sapphire pole, but no alignment of the  $\text{Cu}\langle 110 \rangle$  directions on a specific pole of sapphire, except when the copper interface is exactly parallel to either  $\{311\}$  or  $\{881\}$ .

The existence of a single, strongly preferred OR that is common to copper crystals equilibrated on both the a- and m-planes of sapphire when they are prepared by dewetting in the liquid state raises some interesting questions that we have attempted to answer by performing some additional measurements.

It has been recognized for some time that the “sessile drop” morphology implicit in Young’s equation for wetting equilibrium is too simplistic. Saiz et al. [19] have shown that when a metallic drop is annealed on a flat substrate, a ridge may form at the triple line, in order to allow complete equilibration of surface tension forces. The ridge forms by diffusion, which is driven by forces that are similar to those that operate in the case of grain boundary grooving [20]. In principle, the substrate material that diffuses to form the ridge, originates from both sides of the triple line, i.e. from the drop/substrate interface and from the substrate surface. Ultimately, the interface must reach its equilibrium morphology [21]. In principle, this phenomenon can also take place when the particle is solid. When the interfacial energy is anisotropic, the shape of the substrate beneath the metal drop and/or particle will consist of a faceted crater [22,23].

This type of phenomenon is illustrated in Fig. 4, which displays a SEM micrograph of a sample dewetted in the solid state. The figure shows the imprints left by copper crystals that have evaporated. It also shows the r- and s-plane micro-facets on the free surface of sapphire, illustrated previously in Fig. 1a and c.

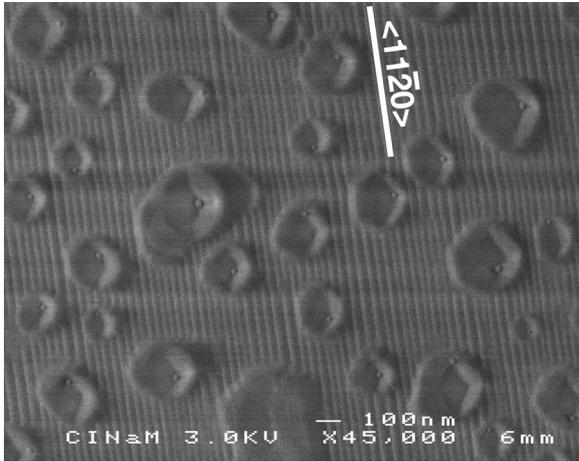
In view of this interface morphology, and the observation that the OR of copper on the m-plane is the same as on the a-plane, one question that immediately arises is whether the particle/substrate interface contains a-plane facets. If it does, then it is conceivable that having copper in contact with a-plane facets, at the copper/sapphire interface of m-plane substrates, might trigger the nucleation of the OR observed on a-plane substrates. However, all our attempts to identify a-plane facets at the copper/sapphire interface by atomic force microscopy were inconclusive.

### 3.2. OR of Cu on r-plane sapphire dewetted in the liquid or the solid states

XRD analysis of the as-deposited copper films on the r-plane substrate showed that the copper grains in the film adopt an OR with a  $\{111\}$  plane parallel to the substrate. When the copper on

\* It may be useful to recall at this point that in the 4-index notation used here for sapphire,  $[hki\bar{l}]$  directions are not generally normal to  $(hki\bar{l})$  planes, except for  $[0001]$  and for directions where  $l=0$ .

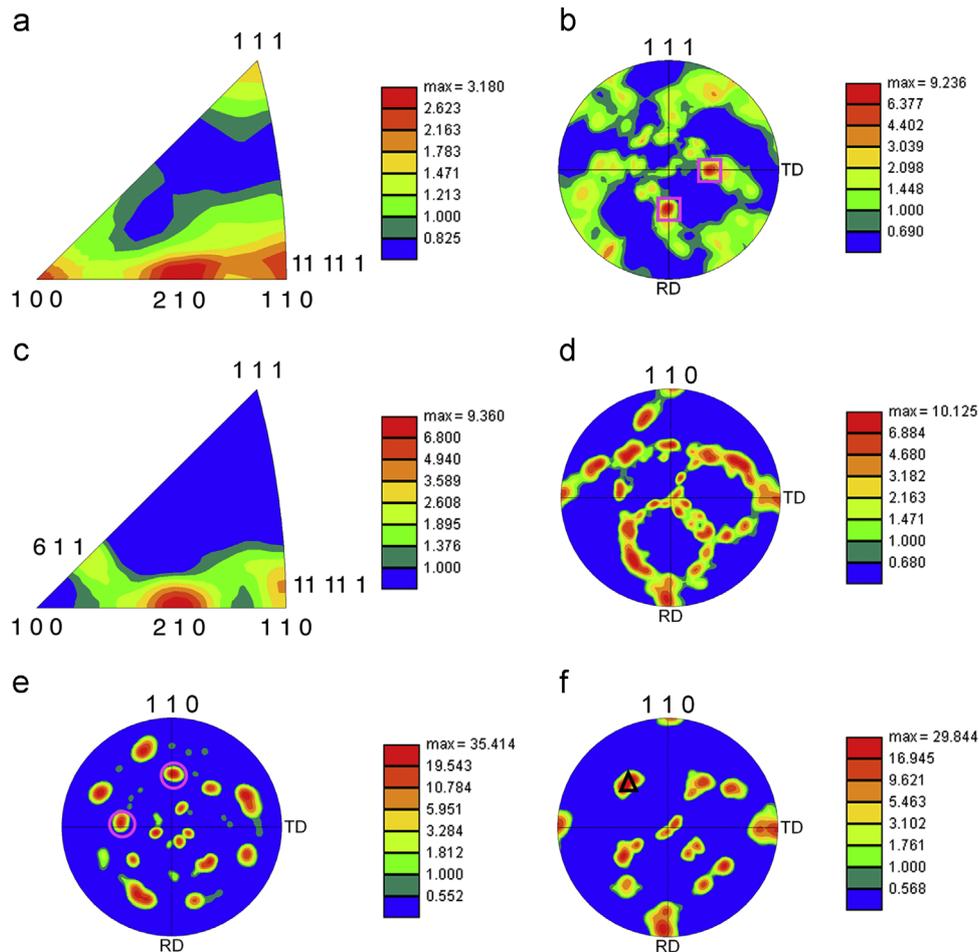
these samples is dewetted in the solid state, the copper crystals retain a preferred  $\{111\}$  plane parallel to the interface, as observed previously for copper crystals on c-plane and a-plane substrates [1,2]. However, when dewetting of copper on the



**Fig. 4.** SEM micrograph of the sapphire m-surface after annealing with copper crystals; each crater marks the location of an evaporated copper crystal; the lines are due to r- and s-micro-facets lying along a  $\langle 11\bar{2}0 \rangle$  direction.

r-plane substrates is performed in the liquid state, the copper crystallizes with preferred  $\{100\}$ ,  $\{210\}$  or  $\{110\}$  planes parallel to the r-plane substrate, as shown in the  $(001)$  IPF of Fig. 5a. Now consider Fig. 5b, which shows the  $\{111\}$  PF of all the 969 Cu crystals present in Fig. 5a. The pink open squares in Fig. 5b represent sapphire  $(11\bar{2}0)$  poles and these are superimposed on the highest frequency Cu $\{111\}$  poles. Out of this population of Cu crystals, we select a subset that displays  $\{111\}$  poles that lie within  $\pm 6^\circ$  of the sapphire  $(11\bar{2}0)$  poles in Fig. 5b. This represents 375 Cu crystals out of a total of 969, i.e. 39% of all the copper crystals. This subset is replotted onto a  $(001)$  IPF in Fig. 5c, and displays interfacial planes with the r-plane substrate that lie along  $\{210\}$ ,  $\{1111\}$  or  $\{611\}$ . Thus, we conclude that the copper crystals with a  $\{100\}$  plane parallel to the substrate, seen in the  $(001)$  IPF of all the copper crystals (Fig. 5a) do not belong to this subset. The  $\{110\}$  PF of the Cu crystals in this subset is shown in Fig. 5d. We proceed to further split the Cu crystals in this subset into two additional subgroups: those with  $\{210\}$  planes parallel to the r-plane substrate, and others with either  $\{1111\}$  or  $\{611\}$  planes parallel to the sapphire substrate;  $\{110\}$  PFs for these two subgroups are shown in Fig. 5e and f, respectively.

In Fig. 5e, the pink open circles, which represent the sapphire  $\langle 1101 \rangle$  directions, are superimposed on the  $\{110\}$  poles of the copper crystals with a  $\{210\}$  plane parallel to the sapphire substrate. By retracing the various superpositions of orientations of copper



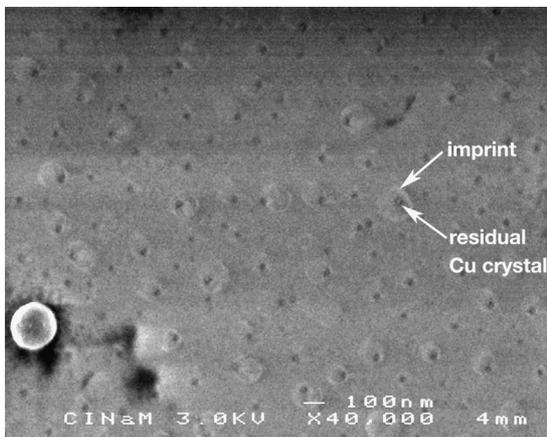
**Fig. 5.** (a)  $(001)$  IPF of 969 copper crystals dewetted from the sapphire r-plane in the liquid state; (b)  $\{111\}$  PFs of all the copper crystals. (c)  $(001)$  IPF of the subset of copper crystals with a  $\{111\}$  direction parallel to a sapphire  $\{11\bar{2}0\}$  pole and (d)  $\{110\}$  PF of these copper crystals. (e)  $\{110\}$  PF of the copper crystals with a  $\{111\}$  direction parallel to a sapphire  $\{11\bar{2}0\}$  pole and a  $\{210\}$  plane parallel to the r-plane; they represent two variants of the same OR. (f)  $\{110\}$  PF of the copper crystals with a  $\{111\}$  direction parallel to a sapphire  $\{11\bar{2}0\}$  pole and a  $\{1111\}$  or  $\{611\}$  plane parallel to the r-plane; they represent two variants of the same OR. On the pole figures the sapphire  $\{11\bar{2}0\}$  poles (open pink squares), and the sapphire  $\langle 1101 \rangle$  (open pink circles) and  $\langle 0001 \rangle$  (open black triangles) directions are also plotted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

crystals in this subgroup with the r-plane substrate, one may conclude that copper crystals display two variants of the same OR, which may be written as  $\text{Cu}\{111\}\langle 110 \rangle \parallel \text{Al}_2\text{O}_3(11\bar{2}0)\langle \bar{1}101 \rangle$ . In Fig. 5f, the black open triangle, which represents the sapphire  $[0001]$  direction, is superimposed (within a few degrees) on the  $\{110\}$  poles of the copper crystals with their  $\{1111\}$  or  $\{611\}$  planes parallel to the substrate. These copper crystals thus also display two variants of the same OR, within a few degrees of:  $\text{Cu}\{111\}\langle 110 \rangle \parallel \text{Al}_2\text{O}_3(11\bar{2}0)[0001]$ . This alignment is the most frequent one for copper crystals on r-plane sapphire, and was observed here for 23% of the total number of copper crystals.

Unlike the results obtained on the m-plane substrates, the sapphire r-plane substrate beneath the copper particles remains essentially flat. Fig. 6 shows faint imprints where the copper crystals have evaporated. These imprints display shallow ridges but the r-plane remains stable beneath the copper crystals, as in the case of the sapphire a-plane [2]. This is an indication that the torques (i.e. the derivatives of the interfacial energy with rotation angle) associated with this copper/sapphire interface are sufficiently large to balance the tendency for the substrate to rotate and form ridges at the triple line [21]. Thus, in this case it is possible to rule out the presence of the a-plane at the copper/sapphire interface, as a rationale for the formation of the preferred OR.

### 3.3. Comparison of the ORs on the a-plane, the m-plane and the r-plane

Since the behavior of Cu on the a- m- and r-planes of sapphire seems related, we focus here on the results obtained on those three substrates. Table 1 summarizes the most frequent planes of Cu which lie parallel to these three sapphire substrates at three stages in the equilibration of Cu crystals with the substrates: the as-deposited state of the Cu film prior to dewetting, and the states after solid or liquid state dewetting.



**Fig. 6.** Imprints of evaporated copper crystals on the r-plane. The darker regions at the top of the micrograph and at the bottom left around the copper particle, are due to charging, since the particle imprints can only be seen on the sapphire surface which has not been carbon coated.

**Table 1**  
A summary of the most frequent Cu planes which lie parallel to three sapphire substrates.

Feature	a-Plane substrate	m-Plane substrate	r-Plane substrate
As-deposited	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(a)$	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(m)$	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(r)$
$\text{Cu}\{hkl\}\parallel \text{Al}_2\text{O}_3(\text{plane})$			
After solid state dewetting	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(a)$	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(a)$	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(r)$
$\text{Cu}\{hkl\}\parallel \text{Al}_2\text{O}_3(\text{plane})$			
After liquid state dewetting	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(a)$	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(a)$	$\text{Cu}\{111\}\parallel \text{Al}_2\text{O}_3(a)$
$\text{Cu}\{hkl\}\parallel \text{Al}_2\text{O}_3(\text{plane})$			

The as-deposited films show a strong tendency for  $\text{Cu}\{111\}$  to lie parallel to the substrate. This type of film texture is common for fcc metals on many substrates. It has even been found for fcc metals on patterned substrates [24]. This suggests that the orientation of the film during the deposition process is driven by the minimization of the surface energy of the copper film, which is the lowest for the  $\{111\}$  orientation. However, when dewetted, the crystallites of Cu may be able to rotate into more favorable ORs, and this clearly occurs in the case of the m-plane substrate where the Cu rotates so as to have a  $\{111\}$  plane parallel to the substrate's a-plane, even though the a-plane may not be present at the interface. When a crystallite rotates into a more favorable OR [25] it can become trapped at a shallow cusp in the spatial variation of interfacial energy, i.e. in some local metastable equilibrium position.

In order to compare the frequency of the preferred OR for copper on each of the a-, m- and r-plane substrates of sapphire, a computer program was used to calculate the smallest angle between all possible  $\{111\}$  planes of a copper crystal and the a-planes of the sapphire substrate, from the Euler angle data recorded during the EBSD experiments [26]. For copper crystals prepared by dewetting in the liquid state, the frequency of this preferred orientation within  $\pm 6^\circ$  was found to be 73%, 65% and 39% on the a-, m- and r-plane substrates, respectively. The complete OR:  $\text{Cu}\{111\}\langle 110 \rangle \parallel \text{Al}_2\text{O}_3(11\bar{2}0)[0001]$  appears with a lowest frequency on the r-plane (23%) but still remains the preferred OR.

When a film is dewetted by passage through the liquid state, its previous history is eliminated, and a new OR can develop by the formation of a favorable solid nucleus on the substrate. Thus, liquid state dewetting is more likely to produce equilibrium ORs. This view seems to be supported by the results of Table 1, which show a further change occurring for Cu on the r-plane substrate: copper crystals with  $\{111\}$  planes parallel to the sapphire r-plane after solid state dewetting, change to having their  $\{111\}$  planes become parallel to the sapphire a-plane after liquid state dewetting. Indeed, all of the substrates listed in Table 1 adopt the same preferred OR after liquid state dewetting:  $\text{Cu}\{111\}\langle 110 \rangle \parallel \text{Al}_2\text{O}_3(11\bar{2}0)[0001]$ , and this OR seems to prevail even when no a-plane may be present at the Cu/ $\text{Al}_2\text{O}_3$  interface.

## 4. Concluding remarks

Thus far, the ORs that develop between copper crystals and sapphire have been studied by similar techniques on four sapphire substrate orientations with surfaces parallel to the c-, a-, m- and r-planes. The preferred OR of copper obtained by liquid state dewetting has been found to be the same on a-, m- and r-plane sapphire substrates:  $\text{Cu}\{111\}\langle 110 \rangle \parallel \text{Al}_2\text{O}_3(11\bar{2}0)[0001]$ . This is in contrast to the behavior of copper on c-plane sapphire, where four different ORs develop as a result of liquid state dewetting. The multiplicity of ORs of copper on the sapphire c-plane has been interpreted as resulting from a degeneracy of the copper/sapphire interfacial energies over the observed range of copper interfacial planes.

Finally, it is worth noting that there has been a comprehensive study of the ORs of Nb on sapphire substrates with surface orientations lying along the c-, a-, m- and r-planes of sapphire [27]. It is interesting to note that for that case of a bcc metal on sapphire, a single OR was observed on all four substrates, and that in all cases the Nb atoms in the first layer adjacent to the interface were found to coincide with the Al-ion sub-lattice. However, although a detailed study of coincidences was made in our previous investigation of the OR of copper on the sapphire a-plane [2], no comparable matching was found in that case.

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