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Characterization of metal films on corundum substrates

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Gold layers on corundum, α-Al_2O_3, substrates, with intermediate sputtered copper and chromium layers, are used for microwave integrated circuit applications. The existance of "islands" of monocrystalline Au and Cu in otherwise polycrystalline material has been verified using X-ray and electron diffraction techniques. In these monocrystalline regions, a discrete Cr layer, under the Au and Cu layers, is no longer present. Investigations on specially prepared samples established the monocrystalline Cu to be a twinned epitaxic layer with $(1\,1\,1)$Cu//$(0\,0\,0\,1)\alpha$-Al_2O_3; $[\bar{1}\,\bar{1}\,2]$ Cu//$[2\,\bar{1}\,\bar{1}\,0]\,\alpha$-$Al_2O_3$. In a sample consisting of a single Cr layer on α-Al_2O_3, the Cr was found to be epitaxic with $(1\,1\,0)$ Cr//$(0\,0\,0\,1)\alpha$-Al_2O_3. Epitaxic "islands" are detrimental to device performance, and their formation has been suppressed by reducing the sputtering power density.

1. Introduction

Gold layers on $\{0\,0\,0\,1\}$ orientation, corundum (α-Al_2O_3) substrates, with intermediate copper and chromium layers, are used for microwave integrated circuit applications. After substrate cleaning, an initial thin (~250 Å) Cr layer is employed to aid the adhesion of the Cu to the corundum substrates. Both the Cr and Cu are deposited using conventional r.f. sputtering techniques. The Cu layer is $\approx 1\,\mu$m thick and is used as a highly conducting base on which Au can easily be electroplated. The Au layer is normally of a thickness not less than $5\,\mu$m which is approximately three times the electrical skin depth at operational frequencies. The use of sputtered Cu, rather than sputtered Au, greatly reduces the unit cost of production for microwave integrated circuit substrates.

Variations in surface texture of the Au have been observed on some samples. In particular, instead of the usual uniform matt appearance some layers exhibited shiny gold patches extending over large areas of the surface. Under an optical microscope, trigonal features were observed in the shiny areas (see Fig. 1), suggesting single crystal "islands" had formed in the otherwise polycrystalline material. Further, it was evident, when viewing through the reverse side of the transparent substrate, that the Cr layer as such was no longer present under the "islands" and Cu was in contact with the substrate.

Samples were examined using a GEC X-ray texture camera [1], and it was confirmed that mono-

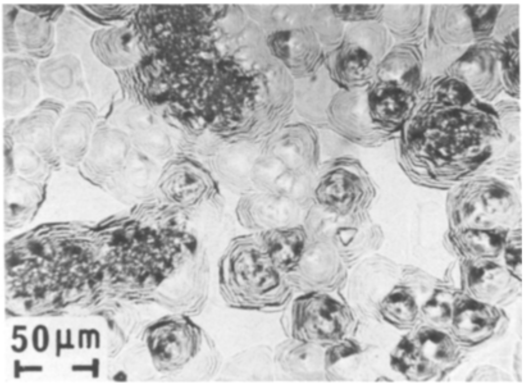


Figure 1 Optical micrograph of "anomalous" layer growth.

crystalline areas had been formed. Special samples, consisting of only one or two metal layers, were then prepared because of the inaccessibility of the Cr and Cu layers to non-destructive X-ray and electron diffraction techniques when the much thicker Au layer is present. These samples were examined in order to determine epitaxic relationships.

2. Experimental

Samples were prepared as follows:

device samples	Au/Cu/Cr/α-Al_2O_3	5 μm Au, electroplated 1 μm Cu, sputtered 250 Å Cr, sputtered

specially-prepared samples:

sample 1	Cu/α-Al_2O_3	1 μm Cu, sputtered
sample 2	Cr/α-Al_2O_3	700 Å Cr, sputtered
sample 3	Cu/Cr/α-Al_2O_3	1 μm Cu, sputtered 250 Å Cr, sputtered.

The device samples represent an early stage in the production of microwave integrated circuits. These are conventionally metallized insulating substrates, in this case single crystal α-Al_2O_3, which are then etched using photolithographic techniques to produce the required microwave circuit.

In all cases the substrates were 1 in. × 1 in × 0.025 in. with polished faces nominally parallel to the basal plane. Coating was achieved in a diode r.f. sputtering system capable of depositing Cr, Cu and Au, although the thicker Au layer is usually electroplated. Cr was deposited at a power density of 8 W in.$^{-2}$ in an argon plasma at a pressure of 6×10^{-3} Torr, and Cu at a power density of 30 W in^{-2}. On sample 3 the Cu layer over part of the surface was etched away; in this way information could be obtained concerning the state of the thin Cr layer.

The samples were examined using the GEC X-ray texture camera, reflection high-energy electron diffraction (RHEED), and back-reflection Laue X-ray techniques. In addition, reflection X-ray topographs were obtained from the Cu layer and substrate of sample 1.

3. Results

3.1. Device samples

As described in Section 1, some of the device samples exhibited variations in surface texture of the Au layer. X-ray texture camera [1] photographs obtained from anomalous shiny and normal matt areas of a slice are shown in Fig. 2a and b, respectively. The Au pattern, which is indexed on the right-hand side of Fig. 2a, is of quite different character in the two cases. Fig. 2b confirms that the matt surface areas consist of polycrystalline Au with very little preferred orientation. Preferred orientation would have been apparent by arcing along the diffraction lines. (The weak diffraction line visible between the 2 2 2 and 4 0 0 Au lines is a spurious reflection from the collimator, whose scatter shield was inadvertently left off.)

The Au layer in the shiny surface region consists of a high proportion of monocrystalline material, as evidenced by the pattern in Fig. 2a. In X-ray texture camera photographs the charac-

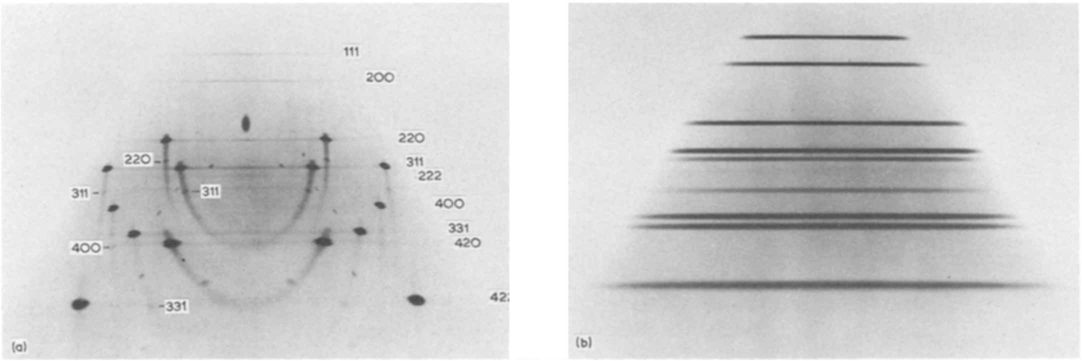


Figure 2 GEC X-ray texture camera photographs of a device sample. Ni-filtered Cu radiation; $i = 30°$; continuously rotated. (a) "Shiny" area, (b) matt area.

teristic spots from a monocrystalline phase still lie on the corresponding powder lines. White radiation streaks, observed crossing the powder lines, are formed because the (monocrystalline) sample is continuously rotated and represent lines of constant α, where α is the angle between a particular Bragg plane and the surface plane. The values of α, which can be read from a prepared chart, for each Au reflection in Fig. 2a are consistent with a proposed $\{1\,1\,1\}$ orientation, i.e. $\{1\,1\,1\}$ Au parallel to the surface. The 1 1 1 or 2 2 2 characteristic reflections would then be recorded only if the angle of incidence, i, was set equal to the Bragg angle for that reflection, since the rotation of the sample is about the surface normal. For Fig. 2a $i = 30^\circ$ and, therefore, the 1 1 1 and 2 2 2 Cu$K\alpha$ reflections were not excited; the spot visible in the centre above the 2 2 0 Au line is a Laue spot from the (1 1 1) plane.

A second set of spots, much fainter than the Au spots, can be observed to lie on the white radiation streaks. This second pattern has been indexed in Fig. 2a in terms of a monocrystalline copper phase. Au and Cu both possess a face-centred cubic structure. The fact that the Cu spots lie on the Au streaks indicates that the Cu is also oriented with a $\{1\,1\,1\}$ plane parallel to the specimen surface.

A third monocrystalline phase can be observed in Fig. 2a as a pattern of faint spots. These spots have been identified as an α-Al_2O_3 pattern, and can be shown to lie on layer lines consistent with the $\{0\,0\,0\,1\}$ substrate orientation.

Because of the absence of a chromium layer under the monocrystalline gold and copper areas it appeared that the crucial stage in the epitaxy process was the sputtering of the Cu layer. It was thought possible that during the sputtering treatment localized areas of the slice reached temperatures high enough to allow first the Cr to diffuse away from the interface, and then to promote epitaxy of the Cu with the α-Al_2O_3 substrate. The subsequent Au layer would then form epitaxially on the monocrystalline Cu areas. In order to determine in-plane epitaxic relationships, back-reflection Laue photographs were obtained. However, these photographs detected only the relatively thick Au layer. Special samples were, therefore, prepared as detailed in Section 2 (samples 1, 2 and 3).

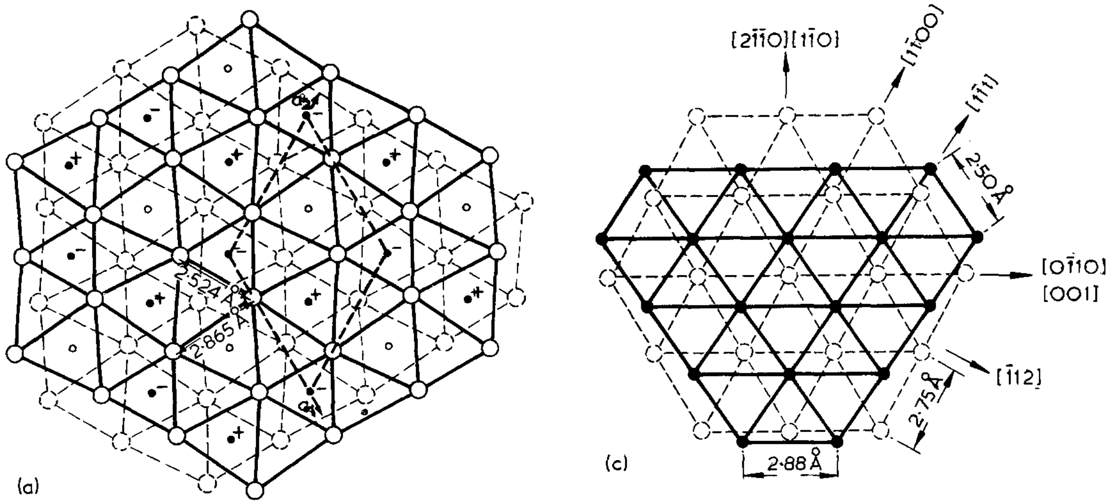
3.2. Cu/α-Al_2O_3

An X-ray texture camera examination of sample 1 revealed that the Cu layer was epitaxic with $(1\,1\,1)$Cu//$(0\,0\,0\,1)\alpha$-Al_2O_3. The in-plane orientation was identified using a back-reflection Laue X-ray technique as $[\bar{1}\,\bar{1}\,2]$Cu//$[2\,\bar{1}\,\bar{1}\,0]\alpha$-$Al_2O_3$. The Laue photographs also showed that the Cu layer was twinned by 180° rotation about the [1 1 1] axis. In this case the substrate was cut 4° off exact basal plane orientation, so that [1 1 1] Cu was tilted 4° away from the surface normal. The above epitaxic condition is identical to that reported for Cu on α-Al_2O_3 by Katz [2].

The origins of the twinned condition can be understood by considering the atomic arrangements in the two lattices near the interface. The α-Al_2O_3 lattice consists of a slightly distorted hexagonal close-packed array of oxygen ions with the smaller aluminium ions occupying some of the octahedral interstices. Adjacent oxygen and aluminium layers, parallel to (0 0 0 1), are shown schematically in Fig. 3a. Two-thirds of the available interstices are filled by aluminium ions. If the α-Al_2O_3 structure is considered as hexagonal close-packed, the oxygen layer sequence is ABAB . . . and the Al sites are C sites. It is assumed that the epitaxy is that of a close-packed plane of the f c c metal (ABCABC . . . stacking) on a close-packed oxygen plane.

Twinning occurs because the stacking sequence of the initial Cu layers is not unambiguously governed by the substrate. Interfacial oxygen and Cu layers are shown schematically in Fig. 3b, with Cu ions occupying C sites (i.e. sites which would be occupied by Al ions in α-Al_2O_3). The misfit is −7%, while the possible presence of substitutional Cr atoms in the Cu lattice would tend to improve the fit. Twinning would be promoted by the second Cu layer occupying alternative A and B positions, leading to CAB and CBA sequences. It is also possible that the first Cu layer could occupy alternative C and A positions (see Fig. 3b), again leading to twinned sequences.

In order to gain evidence of the crystalline development of the Cu layer, reflection X-ray topographs were obtained, using a Lang camera (see, for example, [4]), from the substrate and layer of sample 1. The topographs are shown in Fig. 4. The diffraction peak from the layer, as monitored during the setting-up of the topograph, was very broad compared with the substrate reflection (order of magnitude difference in half-height width of the profile). Prominent linear features visible in the substrate topograph (Fig. 4a)



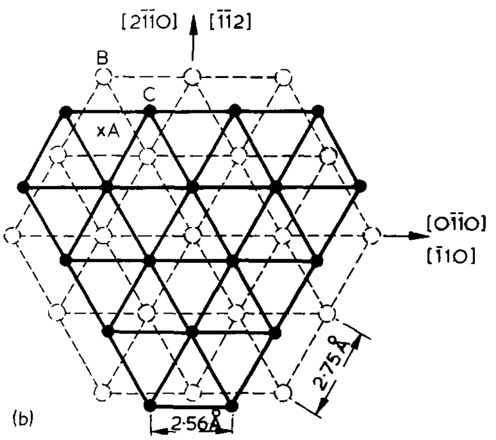


Figure 3 (a) α-Al$_2$O$_3$ structure.
Key: ◌ first oxygen layer (height $c/12 = 1.083$ Å)
○ second oxygen layer (height $c/4 = 3.248$ Å)
$\bullet^+$ Al ion at height 2.404 Å
$\bullet^-$ Al ion at height 1.923 Å
∘ hole at height 2.170 Å
--- outline of unit cell (heavy dashed lines).
(b) Atomic configurations of Cu and α-Al$_2$O$_3$ in interfacial plane. Oxygen layer shown as undistorted hexagonal array.
Key: ◌ oxygen atoms (0 0 0 1) plane
● copper atoms (1 1 1) plane.
(c) Atom configurations of Cr and α-Al$_2$O$_3$ in interfacial plane.
Key: ◌ oxygen atoms (0 0 0 1) plane
● chromium atoms (1 1 0) plane.

are due to polishing scratches. An array of short linear features, interpreted as dislocation images, is also visible over a large part of Fig. 4a. Although the definition of features in the layer topograph (Fig. 4b) is poor, some X-ray extinction is taking place as evidenced by the imaging of some scratches. The scratches existing on the substrate surface have influenced the growth of the layer; for example, the two parallel, diagonal scratches imaged in Fig. 4a are visible near the right-hand side of Fig. 4b. No evidence of twinning is seen in Fig. 4b, although only one of the twinned components contributes to a 2 2 0 reflection topograph. The twinning appears to be on a sub-micron scale.

3.3. Cr/α-Al$_2$O$_3$

Although the Cr layer on device samples was found not to be present under the monocrystalline layer areas, and therefore does not participate directly in the epitaxy process, it was of interest to examine a single Cr layer on α-Al$_2$O$_3$. At 700 Å the layer was somewhat thicker than that employed for device samples. X-ray texture camera photographs showed that the Cr, of b c c structure, was epitaxic with (1 1 0) parallel to the substrate plane. RHEED patterns obtained from the Cr layer revealed two different in-plane orientations. One of the epitaxic relationships, $[1\,\bar{1}\,0]$Cr//$[2\,\bar{1}\,\bar{1}\,0]$ α-Al$_2$O$_3$, is depicted in Fig. 3c. The other relationship identified was $[\bar{1}\,1\,2]$Cr//$[2\,\bar{1}\,\bar{1}\,0]$$\alpha$-Al$_2O_3$. In both cases, however, there was found to be a range of Cr orientations ~10° on each side of these mean orientations. A possible explanation of this spread in orientation is that the close-packed Cr ⟨1 1 1⟩ directions are tending to align with the close-packed substrate ⟨1 0 $\bar{1}$ 0⟩ directions. Three-fold twinning of the layer is also expected to occur, imposed by the [0 0 0 1] triad substrate axis, which is not duplicated in the layer. These two phenomena would account for the observed RHEED patterns.

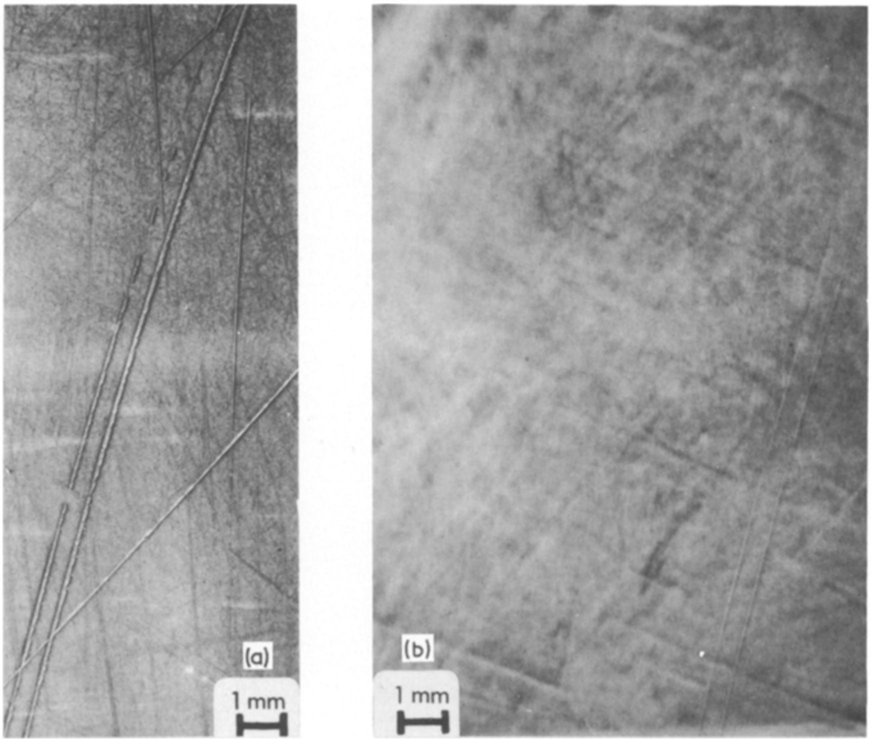


Figure 4 (a) $1\,1\,\bar{2}\,9$ reflection topograph of α-Al_2O_3 substrate (sample 1); Cu$K\alpha$ radiation. (b) $2\,2\,0$ reflection topograph of Cu layer (sample 1); Cu$K\alpha$ radiation.

A small quantity of polycrystalline Cr, with a ⟨1 1 1⟩ preferred orientation, was also detected in the RHEED patterns.

3.4. Cu/Cr/α-Al_2O_3

Both layers in sample 3 were found to be polycrystalline, and both films appeared to be continuous. It appears, therefore, that in this case the temperature required for the epitaxy process to proceed was not attained. In this respect it should be noted that epitaxy occurred on only some device samples.

4. Discussion

During sputtering the substrates are heated by electron bombardment and it is likely that bulk temperatures in excess of 200° C are reached, although the surface temperature may be higher. It appears that localized areas of the substrate reach temperatures high enough for the Cr to diffuse into the Cu (or possibly into the α-Al_2O_3) and then for the Cu to form epitaxially on α-Al_2O_3. Examination of the Cu/α-Al_2O_3 sample has enabled the epitaxic relationships to be identified as $(1\,1\,1)$Cu//$(0\,0\,0\,1)\alpha$-Al_2O_3, $[\bar{1}\,\bar{1}\,2]$Cu//$[2\,\bar{1}\,\bar{1}\,0]$ α-Al_2O_3, with the Cu twinned by 180° rotation about $[1\,1\,1]$. This twinning was found to be on a sub-micron scale on the specially prepared Cu/α-Al_2O_3 sample. In device samples it is throught that each "island", of dimension $> 1\,\mu$m, consists of one of the two possible twinned arrangements.

The Cu/α-Al_2O_3 epitaxic condition reported here agrees well with that reported by Katz [2]. It is interesting that Katz [3] found that good epitaxic films were produced at a substrate temperature of 240° C and above, whilst below 240° C increasing randomness of the crystallites in the films was observed as the temperature decreased. It is quite possible that temperatures of this order are achieved during sputtering of the present samples.

When epitaxy occurs on device samples the metallic grain size is large compared to the surrounding polycrystalline material. Since the attenuation of microwaves increases sharply in conductors as the thickness approaches or becomes less than the skin depth ($\sim 2\,\mu$m), excessive microwave loss is introduced by the many deep valleys which occur over the areas of anomalous growth. In order to produce completely polycrystalline layers the source of substrate heating has been reduced by using a sputtering power density of 15 W in.$^{-2}$, instead of 30 W in^{-2}, for Cu. Further, the thickness of the Cr layer has been increased to 500 Å. No instances of epitaxic growth have been found since these processing changes were introduced.

References

1. C. A. WALLACE and R. C. C. WARD, *J. Appl. Cryst.* 8 (1975) 255.
2. G. KATZ, *Appl. Phys. Letters* **12** (1968) 161.
3. *Idem, J. Mater. Sci.* **5** (1970) 736.
4. G. A. ROZGONYI and D. C. MILLER, *Thin Solid Films* **31** (1976) 185.

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