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Mechanical and structural properties of electrodeposited copper and their relation with the electrodeposition parameters

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Abstract

Thin copper-electrodeposited films have been prepared on steel substrates from an additive-free copper sulfate bath by applying different current signals such as rectangular and square wave pulses, triangular waveform and also by direct current with variation of its magnitude.

Mechanical properties of these films have been studied by means of dynamic microindentation measurements known as the universal microhardness test. Values of the hardness, plastic component, Young's modulus and percent of elastic recovery have been measured. In order to obtain the preferential orientation and grain size of the electrodeposits, X-ray diffraction studies have been made as well as scanning electron microscopy to evaluate their morphology. All the deposits showed a preferential orientation but without a simple correlation with the mechanical features of the films. The influence of current density on microhardness through its effect on grain size has been found to obey the Hall–Petch relationship in the nanometer range. Finally, correlations between the mechanical properties of the electrodeposits and the electrodeposition parameters have been made. These kinds of studies raise the possibility of tailoring films with good mechanical performance for different technological applications just by selecting the appropriate electrodeposition conditions.

Keywords: Electroplating; Copper; Microhardness

1. Introduction

Copper is one of the metals most extensively used in industry, either because of its intrinsic properties or as a base to further formation of metallic films. Electrodeposition is one of the methods most generally employed to obtain metallic films of adequate thickness, porosity-free structure and good adhesion [1–3]. Electrodeposited copper films have been widely investigated with respect to their morphological characteristics, electrical properties and corrosion resistance [4,5] but less attention has been paid to their mechanical behaviour and its relation to electrodeposition parameters. By controlling variables such as current density, applied current signal, temperature, bath composition, etc., a variety of films with different characteristics can be achieved, thus allowing to tailor the mechanical characteristics of the coatings for specific applications.

It is well known that one of the ways to control the structure of the electrodeposits is to adjust the current density during dc plating or to apply a periodically changing current signal. In the first case, films of different grain sizes can be achieved, even in the nanometer range if sufficiently high current densities are applied. These nanostructured materials have recently attracted great attention due to the improvement produced specially in the mechanical response (e.g., wear resistance) of the films [6,7]. In the case of a periodically changing current, i.e., periodic electrolysis, different morphologies can be obtained. It has been established that this kind of electrodeposition technique leads to beneficial morphological effects such as smoother, more uniform and more compact deposits [8–10]. This being the case, if different structures showing suitable morphologies can be formed, different and maybe better mechanical responses will be found.

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Regarding the measurement of the hardness of materials, several methods such as the Vickers, Rockwell or Brinell indentation tests have been traditionally used. The difference among them resides in the geometry of the indenter and in the range of employed loads. However, these kinds of tests have resulted to be less accurate than the new universal microhardness test. Several inaccuracies have been discussed, for instance, in relation with the widely used Vickers test [11]:

(a) it is a static method where a constant load is applied, being the hardness number measured upon removal of the indenter, which loses information about the elastic behaviour of the material;
(b) it is made the assumption that the permanent indentation imprint is a true geometric image of the indenter, which is not justified because elastic stresses produced under load are highly nonuniform so the resultant geometry is distorted; and
(c) more important becomes the fact that this imprint has to be measured (by means of a microscope) to find the resulting hardness number.

It is in this point that a significant measurement uncertainty, based on the subjective operator interpretation, is made.

Recent advances in instrumentation allow to measure the mechanical properties of thin films with the advantage of not being subjected to the problems described above. That is the case of the universal microhardness test in the range of microloads, which gives accurate values of the hardness of electrodeposited metallic films. Because hardness is measured with a microindentation, the damage to the surface is minimal and the method can be regarded as virtually nondestructive. This test is based on the measurement of the indentation depth under dynamic load and for a controlled load–unload cycle [12]. It provides understanding not only of the total hardness of the test specimen but also of its plastic component, Young's modulus and percent of elastic recovery. These parameters can be obtained as a result of the particular design of the test. As load is being applied; that is, the indenter is pressed on to the specimen's surface, depth is being measured so both plastic and elastic components are present which, by differences in the load–unload cycle, can be evaluated individually.

Concerning structural features, it is well known that mechanical characteristics of materials are intimately related to their structure, not only through effects of grains and grain boundaries but also through the preferred orientation of the deposits. It has been found that the electroplating conditions also affect the crystal orientation of electrodeposits [13,14], having this been correlated with their mechanical properties [15].

As it is well known, different electrochemical deposition techniques and/or different composition of the solution bath (additives, pH, temperature, etc.) induce film deposits with different physical and mechanical properties. The aim of this paper is to study the influence of the electrodeposition parameters and applied current program and current density on the mechanical characteristics of the electrodeposited copper films, to find the best conditions for specific applications and to correlate hardness and other mechanical values with the structure and morphology of the electrodeposits. In order to simplify the system, we have studied the copper deposition from an additive-free sulfate bath under galvanostatic and pulse conditions.

2. Experimental

Copper electrodeposits were prepared from an additive-free acid copper sulfate bath (composition as follows: 0.8 M $CuSO_4{\cdot}5H_2O$ and 0.4 M H_2SO_4) in ultrapure distilled MilliQ water at room temperature and under moderate agitation. A two-electrode electrolytic cell was used, being stainless steel (1 cm^2) the substrate for the copper electrodeposition and a pure copper foil (18 cm^2), the anode. The electrodeposition was conducted under galvanostatic regime, with a Solartron 1235 galvanostat, both under dc conditions with different current densities, and by applying a periodically changing current signal. Details of the different waveforms generated and current densities employed are shown in Table 1. The cathodic peak current density was always maintained at 6 A dm^{-2}. Cathodic and anodic times (frequency), as well as anodic current density, were selected so that the rate between cathodic and anodic charge was 5:1. The overall electrodeposition times were chosen so that the same amount of net charge was passed.

Table 1
Applied current programs, electrodeposition times and measured thickness of the copper deposits

Applied program	i_c (A dm^{-2})	i_a (A dm^{-2})	t_c (s)	t_a (s)	Electrodeposition time (min)	Thickness (μm)
Rectangular	−6	6	5	1	10.5	6.7
Square	−6	1.2	5	5	25	8.0
Triangular	−6	2.6	5	2.2	25	7.4
dc	−0.6	–	–	–	70	7.4
dc	−6	–	–	–	7	8.5
dc	−12	–	–	–	3.5	5.6
dc	−24	–	–	–	1.7	4.9
dc	−50	–	–	–	0.8	4.4

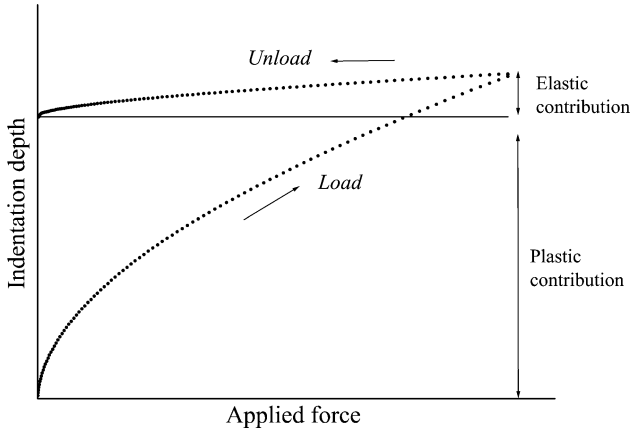

Fig. 1. Typical plot of the indentation depth vs. the applied load obtained with the universal microhardness test.

Electrodeposit thickness, also listed in Table 1, was measured by means of X-ray fluorescence with a Fischerscope X-ray System XUVM equipment. Microhardness characterization was carried out with a Fischerscope HV 100 tester with Vickers indenter and a final test load of 1000 mN stepwise applied. Hardness value (*HU*) is calculated according to the following formula which takes into account the indenter's imprint as a function of the penetration depth [12]:

$$HU = \frac{F}{26.43 \cdot h^2} \quad (1)$$

where F is the applied load in mN and h the penetration depth.

Fig. 1 shows a typical load–unload curve in which zones corresponding to plastic and elastic component of the total deformation are depicted. The area defined between the increasing and decreasing load curves represents the amount of mechanical work done when material flow occurs as a result of the applied load. The unload curve depends only on the elastic properties of the material and values of the Young's modulus (E) are obtained from the slope near the maximum test load.

Morphological characterization was made with a Philips XL30 scanning electron microscope and structural determination by means of X-ray diffraction with a SIEMENS D5000 diffractometer (CuK_α radiation λ = 1.540589 Å).

3. Results and discussion

3.1. Influence of the applied current program on the morphology, mechanical response and structure of the electrodeposited films

3.1.1. Morphology of the deposits

A variety of morphological patterns for the electrodeposits obtained with different current programs and direct current (for comparative purposes) is found. Fig. 2 shows the SEM micrographs of the copper electrodeposits. A fine-grained and compact surface is observed when dc current is applied (Fig. 2a) and a larger grained structure is obtained when rectangular and square current pulses are applied leading to a rougher surface with cracks or crevices (Fig. 2b,c). Finally, the triangular waveform produces a deposit made of grain conglomerates, a cauliflower-like appearance, decreasing considerably the compactness (Fig. 2d). These results do not seem to agree with some literature that reports an improvement in morphology by the periodic electrolysis [8–10]. In our case, it should be pointed out that this kind of improvement was not achieved, at least, with the parameters (I_{peak}, pulse frequency, etc.) used. This could be due to the chosen frequency, which was rather low, and then it could be close to the limit of the dc behaviour. However, if the same cathodic peak current density is employed in all cases (6 A dm^{-2}), the best morphology is that of the deposit obtained under dc conditions which also has the advantage of being straightforward.

3.1.2. Mechanical properties

Mechanical parameters such as the Universal microhardness (*HU*), its plastic component (*HU*), Young's modulus (E) and elastic recovery (W_e) corresponding to the copper electrodeposits obtained with different current programs and also dc current, are shown in Table 2. Fig. 3 shows the microhardness profile of the films. Several conclusions can be drawn from the plot:

(a) the dc and pulse methods produce films with higher microhardness values compared to a metallurgical copper foil (1,3 GPa), not being the case of the triangular waveform;
(b) the dc and rectangular pulse method lead to a homogeneous deposit evidenced by the constant line, while for the square and triangular waveforms, an increase in the value of the hardness with load is observed which is an indication of their lack of homogeneity in "bulk"; and
(c) superficial effects are evidenced from the rising part of the profiles in all the cases.

This is because rougher deposits are obtained, compared with other physical techniques.

With respect to the plastic component of the microhardness, Fig. 4a shows that the hardest deposit corresponds to that obtained under dc conditions while the softest one is obtained when a triangular waveform is used. This fact correlates with the morphological characteristics of the dc deposit (compact appearance and fine grained) in opposition to the other deposits with much coarser grains and less-compact morphology. However, hardness rather than an intrinsic property of a material is a measure of its resistance to localized plastic deformation by means of an indentation test. Therefore, for certain applications, this value is not the

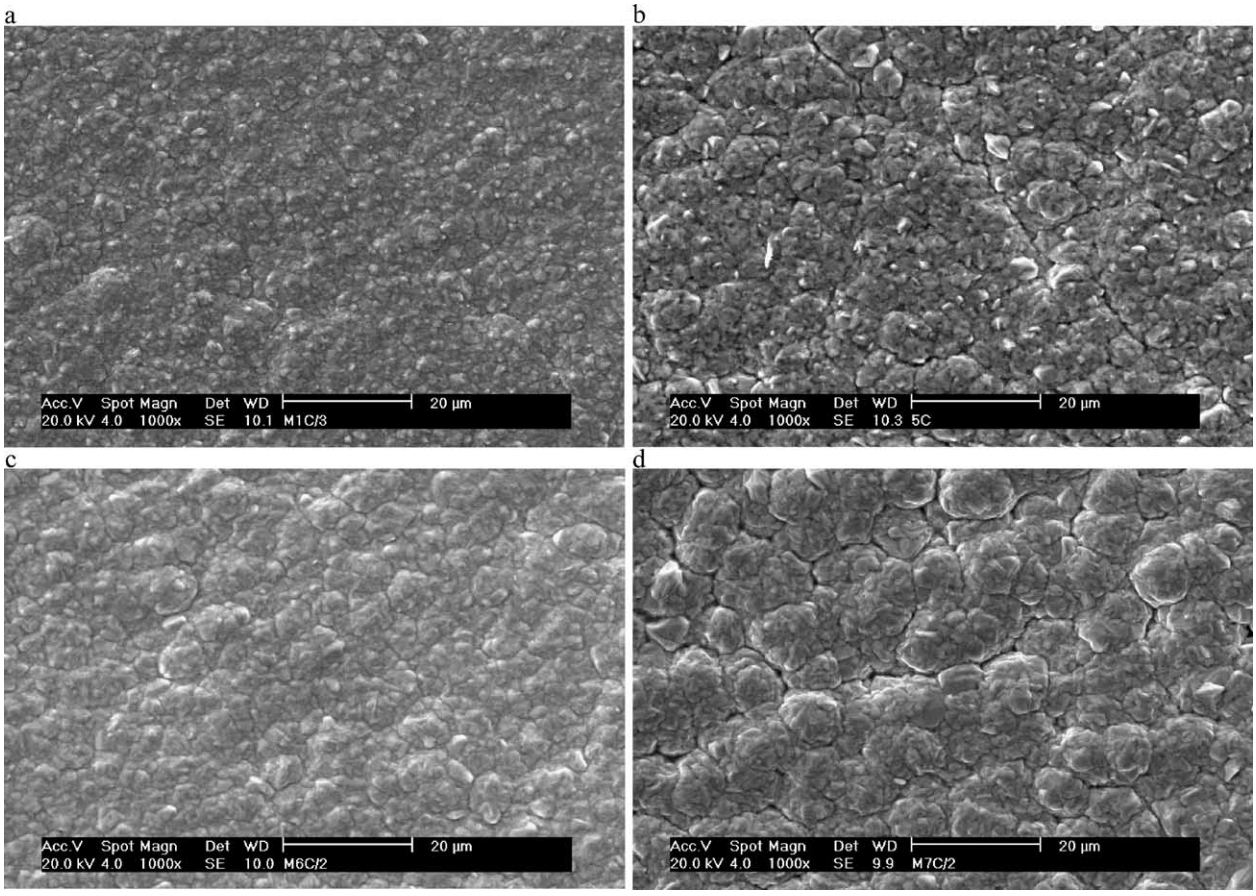

Fig. 2. SEM micrographs of the copper electrodeposits (a) direct current, (b) rectangular pulse current, (c) square pulse current and (d) triangular waveform.

only one that gives us an idea of which is the material that renders the best mechanical behaviour. Other mechanical parameters, such as Young's modulus, have to be taken into account. Fig. 4b shows the Young's modulus values for the different conditions where it can be seen that the rectangular pulse produces films with the highest elasticity.

For some cases, a more general relationship has been proposed to ascertain the mechanical resistance of a material through the ratio between plastic hardness and effective elastic modulus ($E^* = E/(1-\nu^2)$, where ν is the Poisson's ratio) [16–18]. The higher the ratios H^3/E^{*2} and H/E^* are, the better is the mechanical response of the film. Plots of these relations (Fig. 5a,b) point out that the maximum value is that of the rectangular film, not as hard as the one prepared with direct current but more elastic. Other relations can be plotted as well, being the following an intuitive one.

Table 2
Mechanical parameters of the electrodeposited copper films as a function of the applied current program and current density

Sample characteristic	H_U (GPa)	E (GPa)	W_e (%)	H_U plastic (GPa)
Direct current	1.74 ± 0.04	188 ± 36	9.1 ± 1.5	1.83 ± 0.03
Rectangular pulse	1.50 ± 0.02	92 ± 18	14 ± 1.8	1.70 ± 0.06
Square pulse	1.49 ± 0.05	131 ± 7	11 ± 0.6	1.61 ± 0.06
Triangular waveform	1.17 ± 0.1	191 ± 14	6.6 ± 0.2	1.20 ± 0.1
dc 0.6 A dm^{-2}	1.11 ± 0.09	57 ± 3	16.5 ± 1.2	1.29 ± 0.1
dc 6 A dm^{-2}	1.74 ± 0.04	188 ± 36	9.1 ± 1.5	1.84 ± 0.03
dc 12 A dm^{-2}	2.02 ± 0.1	201 ± 15	9.6 ± 1.2	2.15 ± 0.1
dc 24 A dm^{-2}	0.93 ± 0.04	23 ± 0.9	33 ± 0.7	1.38 ± 0.08
dc 50 A dm^{-2}	0.56 ± 0.01	87 ± 0.5	8.4 ± 0.3	0.57 ± 0.01

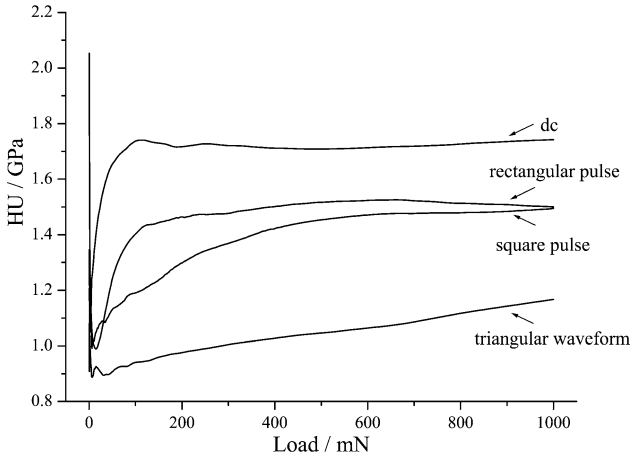

Fig. 3. Universal microhardness profile of the copper films obtained with different current programs.

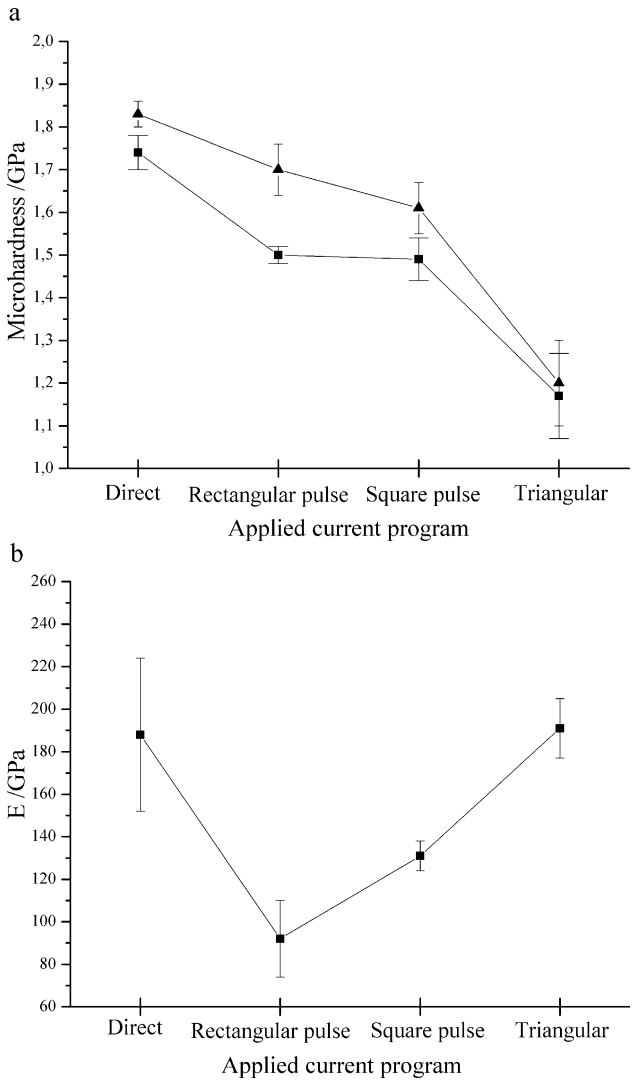

Fig. 4. Mechanical parameters of the copper films obtained with different current programs. (a) Universal microhardness (■) and plastic component (▲), (b) Young's modulus.

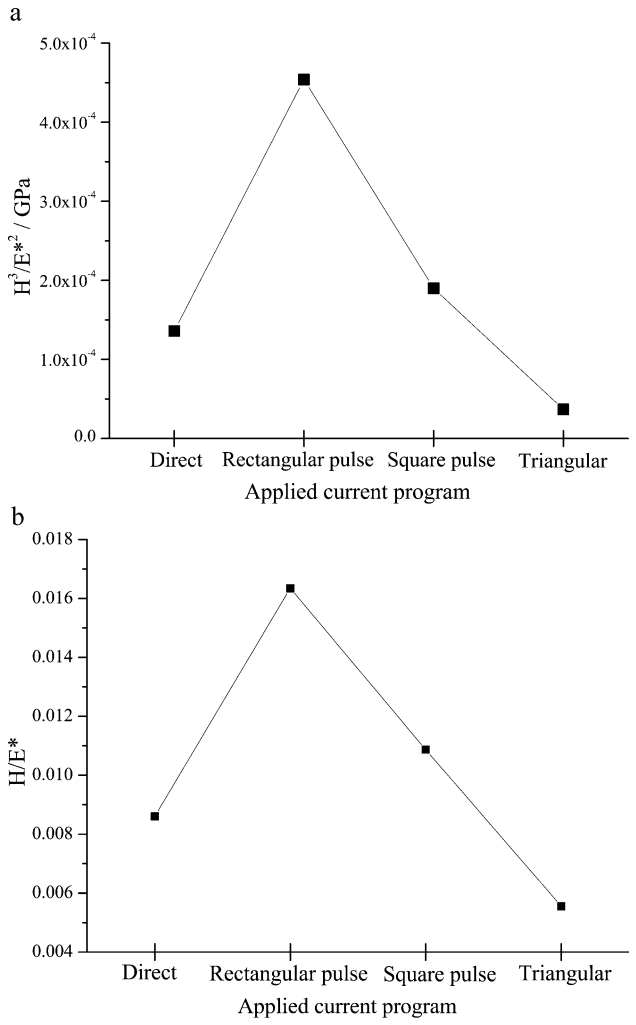

Fig. 5. Variation of the ratio H^3/E^{*2} (a) and H/E^* (b) for the copper deposits as a function of the applied current program.

If the plastic hardness versus E is plotted as in Fig. 6, four quadrants can be assigned considering the values measured on a metallurgical copper foil as a reference ($HU_{pl} = 1.4$ GPa and $E = 110$ GPa). The films with the best mechanical performance, in the sense discussed above, will be those situated at the second quadrant, depicted as a dashed zone in the figure. The worst will be at the fourth one, where, in this case, the point corresponding to the film obtained with the triangular waveform is placed.

3.1.3. Grain size and preferential orientation

X-ray diffractogramms (XRD; Fig. 7) for the copper electrodeposits were obtained. Table 3 shows the variation of grain size (d) evaluated from the broadening of the (111) peak according to Scherrer's formula [19].

While varying current density is known to affect grain size, it can be observed in Table 3 that the deposits obtained with different current signals have rather similar grain sizes

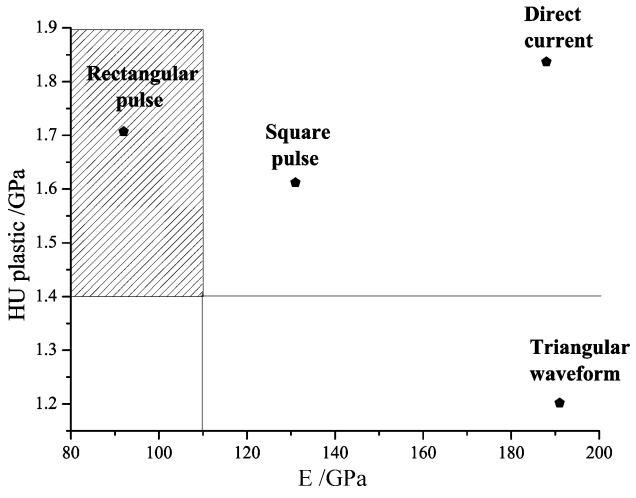

Fig. 6. Plot of the plastic component of the microhardness vs. E for the copper films obtained with different current programs.

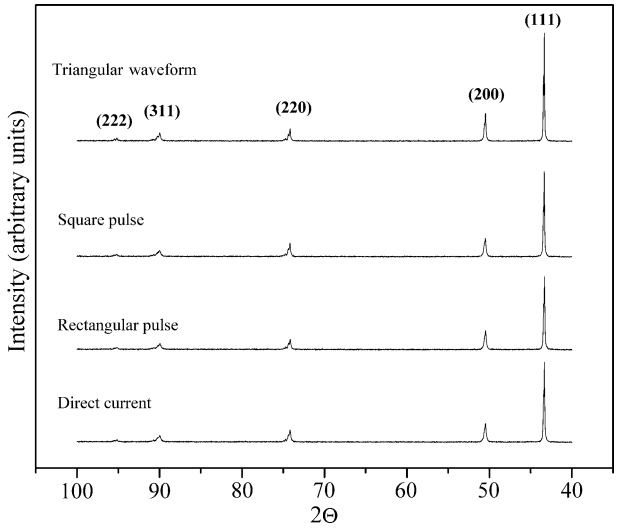

Fig. 7. XRD patterns of the copper electrodeposits obtained with different current programs.

presumably because the same average cathodic current density is maintained. So the increase in the hardness value cannot be attributed exclusively, in this case, to a grain size effect. It should also be noted that the grain size of the films lies within the nanometer range, hence the higher hardness values of the electrodeposited films compared with the metallurgical copper.

Preferential orientation of the films was studied through the evaluation of the orientation index (M) [15]. For each plane, (110) for example, the orientation index is calculated as follows:

$$\mathrm{IFR}(110) = \mathrm{IF}(110)/\{\mathrm{IF}(110) + \mathrm{IF}(200)\ldots\} \quad (2)$$

$$\mathrm{IR}(110) = I(110)/\{I(110) + I(200)\ldots\} \quad (3)$$

$$M(110) = \mathrm{IR}(110)/\mathrm{IFR}(110) \quad (4)$$

where IF(110) is the X-ray diffraction intensity in the JCPDS cards and I(110) is the intensity in the experimental data.

Table 3
Grain size of the films evaluated from the Scherrer's formula, (111) peak

Sample characteristic	d (nm)
Direct current	91
Rectangular pulse	89
Square pulse	85
Triangular waveform	105
0.6 A dm^{-2}	146
6 A dm^{-2}	91
12 A dm^{-2}	80
24 A dm^{-2}	72
50 A dm^{-2}	68

If M has a positive deviation from 1, it indicates a preferential orientation of that plane. On the contrary, it indicates depression in orientation if M is lower than this value. A (222) preferential orientation is found in all cases (Fig. 8), being noticeable a similar tendency to that of the hardness plot (Fig. 4a) which could indicate a certain relation between the predominance of this plane and the hardness of the films.

In the light of these results, it can be concluded that the hardest films are those obtained with the dc method. However, if the Young's modulus is also considered the best mechanical performance, from the H/E^* rate is that corresponding to the rectangular pulse. Considering these facts and taking into account that the dc method is much more simple (for further industrial applications), we have carried out a study on the influence of current density in order to find out if there is an optimum value of current density that leads to H/E^* characteristics similar to those obtained with the rectangular pulse.

3.2. Influence of dc current density on the morphology, mechanical response and structure of the electrodeposited films

3.2.1. Morphology of the deposits

Fig. 9a–d shows the SEM micrographs of the films obtained at 0.6, 12, 24 and 50 A dm^{-2} (micrograph corresponding to 6 A dm^{-2} is shown in Fig. 2a). A wide variation of morphological features is obtained, from big crystallites and a nonuniform surface at low current densities (Fig. 9a) to a decreasing grain size situation (Figs. 2a and 9b), and finally, aggregations (Fig. 9c) forming nodular grains of about 5 μm. These variations can be explained in terms of the model of nucleation and growth of crystals in which growth from existing nuclei is favoured at low current densities, while at high current densities, massive nucleation is the predominant effect,

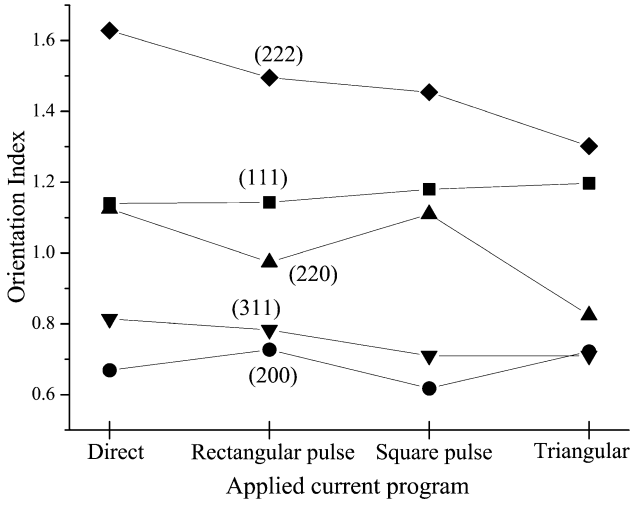

Fig. 8. Variation of the orientation index with the applied current program.

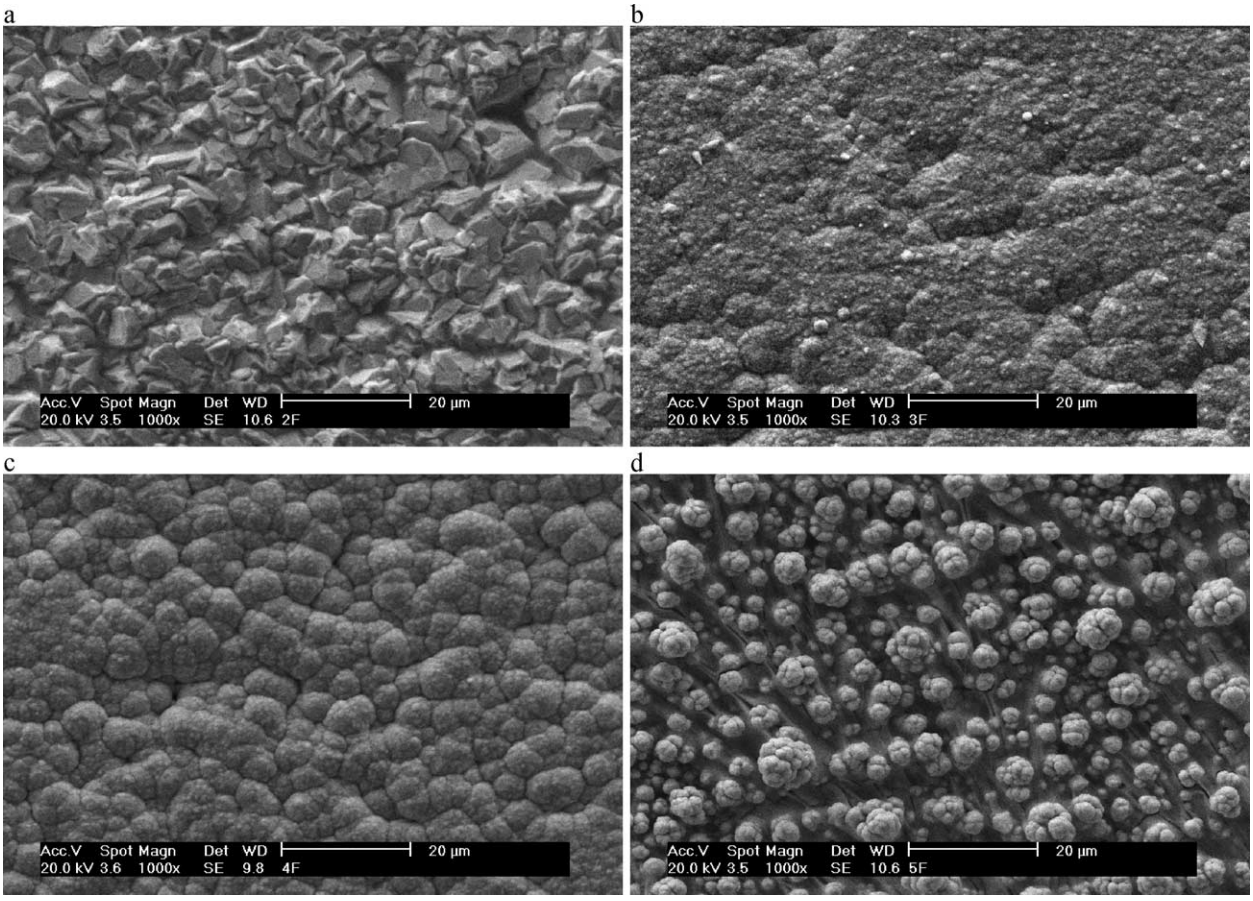

Fig. 9. SEM micrographs of the copper electrodeposits at different current densities (a) 0.6 A dm^{-2}, (b) 12 A dm^{-2}, (c) 24 A dm^{-2} and (d) 50 A dm^{-2}.

thus giving raise to grains of small size. However, at very high current densities, copper deposition becomes mass transfer limited or very close to the mass transfer limit. Whenever this occurs, dendritic and/or powdery deposits result. Therefore, as it can be seen in Fig. 9d, morphology of arborescent grains is found for the deposit obtained at 50 A dm^{-2}.

3.2.2. Mechanical properties

Mechanical parameters measured on the electrodeposits obtained at different current densities are shown in Table 2. Fig. 10a,b shows the change in microhardness and in Young's modulus with current density. At low current densities, the hardness is low but it increases up to a maximum value of 12 A dm^{-2}, followed by a decrease. The same tendency is found for the Young's modulus where the hardest deposits also have a low elasticity, with the exception of that obtained at 50 A dm^{-2} which is both soft and brittle. As in the case of the effect of the applied current program, correlation between these tendencies and morphological features of the deposits can be seen. Hardness ranges from low values, corresponding to a situation where the deposit is not uniform or compact, to the highest values corresponding to a deposit with a fine-grained morphology and compact appearance (6 and 12 A dm^{-2}). Then it decreases because of the formation grain nodules (24 and 50 A dm^{-2}).

As previously discussed, the relations H^3/E^{*2} and H/E^* may constitute a good indication of the mechanical quality of a material. Results shown in Fig. 11a,b again indicates that the best deposit is not the hardest. In this case, the best performance corresponds, by far, to the film obtained at 24 A dm^{-2} where a relative high plastic hardness value is combined with an also high elasticity that leads to higher H/E^* rates which are even higher than those obtained with the rectangular pulse. Response from the other deposits is much lower than this one. This indicates that, although increase in current density leads to harder deposits (up to a certain range), other current densities favour the elasticity and, with an appropriate value of hardness, films with a good H/E^* rate can be obtained.

These results point out a simple way to prepare films, for specific applications, in which adequate values of plastic hardness are combined with a certain degree of elasticity.

3.2.3. Grain size and preferential orientation

X-ray diffractogramms (Fig. 12) were also obtained for the deposits prepared with different current densities. Grain

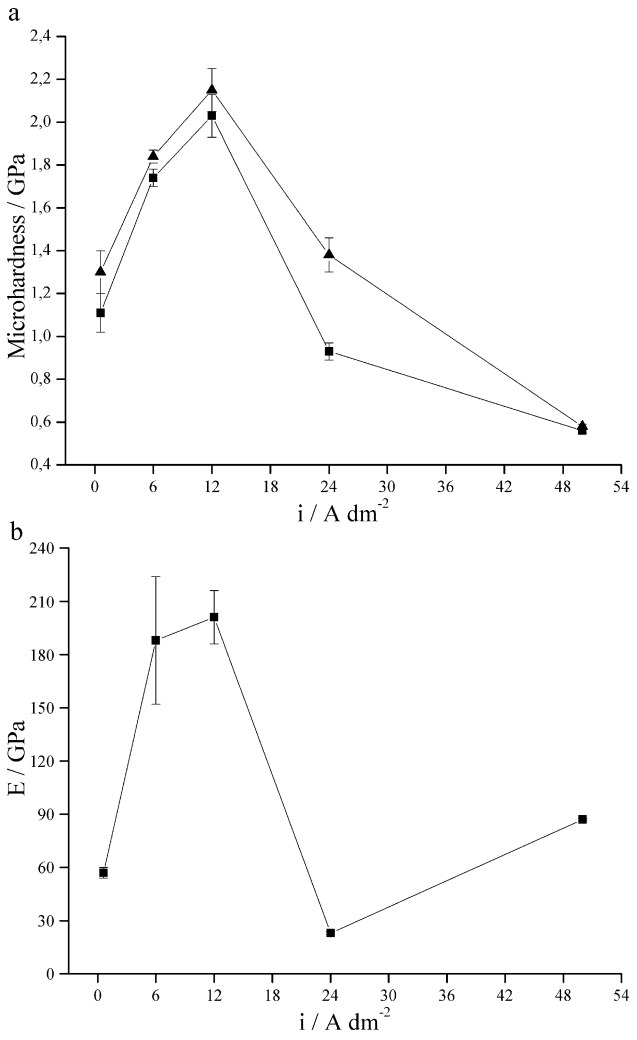

Fig. 10. Mechanical parameters of the copper films obtained at different current densities. (a) Universal microhardness (!) and plastic component (7), (b) Young's modulus.

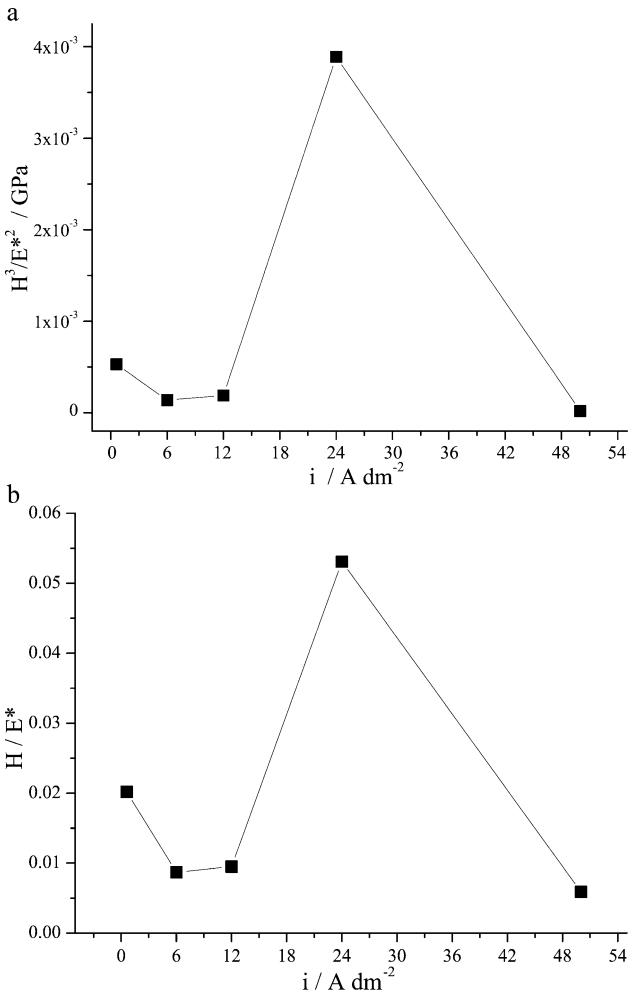

Fig. 11. Variation of the ratio H^3/E^{*2} (a) and H/E^* (b) for the copper deposits as a function of the current density.

size was evaluated, once more, by means of the (111) peak broadening (Table 3), with values lying in the nanometer range. These results show that grain size decreases with increasing current density.

It is well known that an increase in current density (thus promoting the formation of nuclei instead of the growing of crystals) produces a decrease in the grain size and therefore an increment in the observed hardness. This is the described Hall–Petch effect that establishes a linear dependency of the hardness with the reciprocal square root of grain size [20,21]. For the films obtained at different current densities, a Hall–Petch correlation is supported until 12 A dm^{-2} (Fig. 13) which corresponds to the hardness peak value. When the grain size is refined up to the nanometer range, large volume fractions of grain boundaries are introduced, thus producing a strain-hardening effect [22]. The mechanism that gives place to strain hardening relies on restricting the dislo-

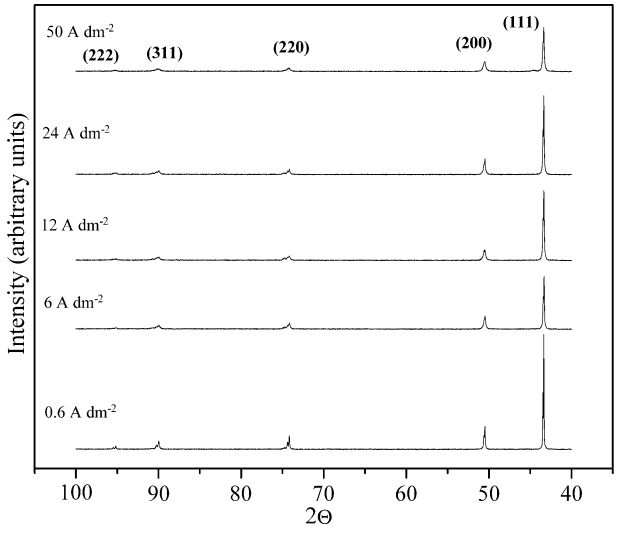

Fig. 12. XRD patterns of the copper electrodeposits obtained at different current densities.

cation motion that occurs by slip or by dislocation at grain boundaries having different crystallographic orientations. Therefore, the Hall–Petch effect is explained in terms of a restriction in the movement of grains, that is, a strengthening due to the formation of pile-ups in the larger grain boundaries associated with low grain size. However, the Hall–Petch relationship has been found to be valid until a certain grain size below which other types of weakening mechanisms begin to play part [23]. The transition from grain-size strengthening to grain-size softening has been attributed to a change in the triple junction (i.e., intersection of three or more grain boundaries) volume fraction. For a certain grain size, the triple-junction volume fraction becomes more grain-size dependent than the grain-boundary volume fraction does. So the onset of the inverse Hall–Petch effect is related to certain values of the triple-junction volume fraction [24]. In our case, the critical value of grain size is around 80 nm. For lower values, an inverse Hall–Petch effect takes place.

Fig. 14 shows the effect of current density on the orientation index. This parameter has been calculated as before. The (111) and (222) planes are the preferred orientations depending on current density. Variation of the orientation index with current density is in this case more noticeable compared with that observed for the variation with the applied current program. As in the case of current program variation, again it can be observed a slight resemblance between the variation of the orientation index corresponding to the (222) plane and the variation of hardness, or even more, of the Young's modulus. Although this could indicate again a certain relation between the predominance of this plane and the mechanical properties, it is not easy to find a simple and straightforward relation; in this case, being the grain size

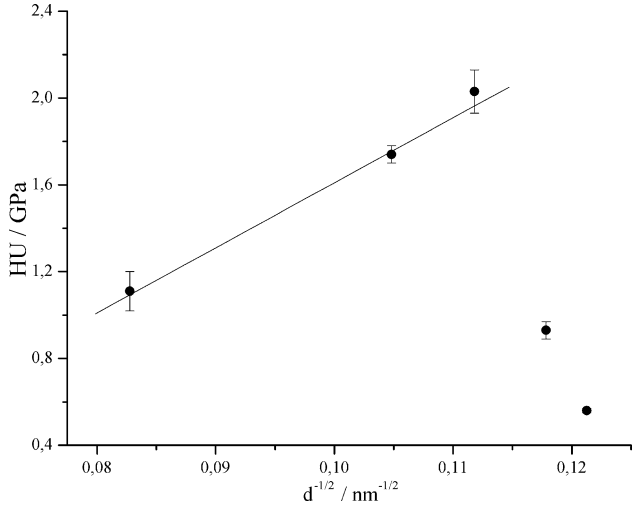

Fig. 13. Relation between microhardness and grain size plotted as the Hall–Petch relationship.

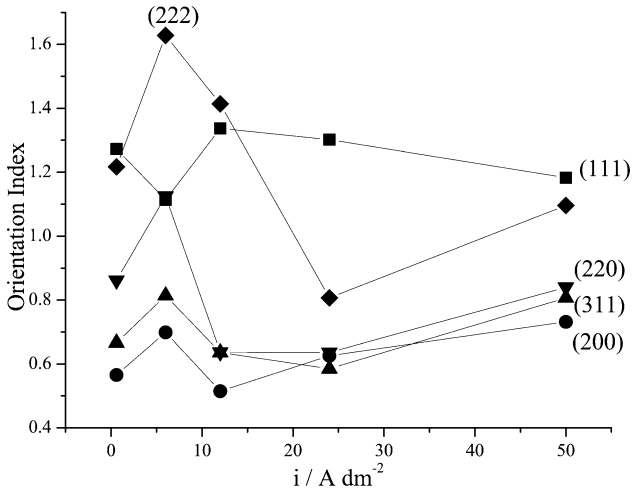

Fig. 14. Variation of the orientation index with the current density.

the most predominant effect over the mechanical behaviour of the films.

4. Conclusions

Relations between electrodeposition parameters and mechanical response have been obtained for the electrodeposited thin copper films. The films with the best mechanical properties are those obtained with the dc and rectangular wave methods. On the contrary, the triangular and square wave methods lead to films with significantly worse characteristics. The hardness values obtained with the dc method were higher than those obtained by application of periodically changing current signals. But concerning elasticity, the rectangular wave method produced better results. However, the adequate selection of the current density leads to deposits with even higher values of hardness and elasticity. The current density that produced the hardest films was found to be 12 A dm^{-2} while the deposit obtained at 24 A dm^{-2} showed the best hardness/elasticity combination. So the optimisation of the current density makes possible to tailor films with specific characteristics for different technological applications.

It has also been found that the grain size of these deposits lies in the nanometer range which permits advantage to be taken of the good properties of these kinds of nanostructures in opposition to the coarse grain materials.

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