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Effects of Cathodic Hydrogen Evolution on Electrodeposited Au-Cu-Cd Alloys

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Hydrogen can be incorporated into electrodeposited Au alloys either during electrodeposition or by cathodic charging. Incorporated hydrogen in these alloys generally impairs their mechanical properties. In this work, we present results of a study of electrochemical, structural, surface composition, and morphological effects of cathodic charging of Au-Cu-Cd alloys electrodeposited from a cyanoalkaline bath. Different kinds of linear sweep voltammetric behaviors are observed for alloys with different compositions and for repeated scans, which is related to a loss of electrocatalytic activity for high Cu content alloys and prolonged cathodic charging. The surface composition of alloys is altered by cathodic charging, resulting in a decrease in Au content. The surface morphology, as observed by scanning electron and atomic force microscopies, is modified by cathodic charging: large crystallites are attacked and globular features appear on flat deposits. The crystallographic structure of the alloys is affected by prolonged hydrogen evolution; the original preferred orientation is disrupted and a Cu-rich phase appears.

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Electrodeposited Au-Cu-Cd has been in consistent use for decorative purposes (practically all of the electroforming of 14 to 18 carat Au hollow jewelry). The electronics industry is also interested in this material (high-performance electric contacts, sliding contacts, slip rings, connectors). The requirements for both electronic and decorative fields strongly stress the mechanical properties of the Au alloy layers (wear resistance, ductility, toughness). It has been proved in previous work[1,2] that hydrogen embrittlement is a major cause of mechanical failure of electroplated Au-based alloys. In this work, we report on compositional, structural, and morphological alterations brought about by hydrogen evolution on electrodeposited Au-Cu-Cd alloys of various compositions.

Accurate but phenomenological studies of Au-Cu-Cd electrodeposited alloys were proposed in the 1970s and early 1980s.[3-5] More recent work is either focused on very specific problems such as pulse plating[6] or is markedly application-oriented. No description is found in the literature concerning hydrogen evolution effects on these alloys, apart from indirect data on cathodic efficiency.[3,4,6] Structural and morphological data are reported for ~18 carat deposits.[4,5] All authors agree on the fact that at least one Au-based disordered solid solution is observed. Steinmann *et al.*[5] report one such phase with strong (111) preferred orientation, while Dettke *et al.*[4] report somewhat doubtful evidence of a polyphasic structure with reflections form four superlattice structures.

Materials and Methods

Baths and electrochemical experiments.—The investigated alloys were electrodeposited with the following bath and operating conditions: Au (as $KAu(CN)_2$) 5 g L^{-1}, Cu (as $KCu(CN)_3$) 50 g L^{-1}, $CdCO_3$ 1.5 g L^{-1}, KCN 20 g L^{-1}, $KHCO_3$ 7 g L^{-1}, and K_2CO_3 5 g L^{-1}, pH 10.5, temp 70°C. Hydrogen evolution experiments were carried out in a 0.125 M aqueous H_3PO_4 solution at pH 6.0 (by NaOH) at 25°C. Electrodeposition of Au-Cu-Cd alloys was carried out galvanostatically (current densities (cd): 2, 5, 10, 20, 50 mA cm^{-2}) in a prismatic cell equipped with a magnetic stirrer. Hydrogen evolution reaction (HER) on Au-Cu-Cd cathodes was studied by linear sweep voltammetry (scan rate 0.5 mV s^{-1}, a Ag/AgCl reference electrode connected to the working electrode via a lateral-channel Piontelli probe and voltages reported *vs.* Ag/AgCl), and by galvanostatic experiments at 10 mA cm^{-2} for 3 h. The electrochemical experiments were carried out under natural convection conditions. The electrokinetic behavior of these baths and the compositional and structural properties of the alloys will be presented in a separate paper.

Structural and compositional investigations.—Electrochemical measurements were complemented by structural and compositional studies. The crystallographic structure of the alloys before and after galvanostatic hydrogen evolution was studied by X-ray diffractometry with powder and thin film goniometers. The surface morphology of the cathodes before and after HER was studied by scanning electron microscopy (SEM), atomic force microscopy (AFM), and laser interferometric profilometry, and the composition was measured by energy dispersive spectroscopy (EDS) (EDS measurements were replicated four times for each sample). Hydrogen release from cathodically charged samples was studied by the LECO technique.[7]

Results and Discussion

HER linear sweep voltammetry experiments.—Cathodic linear sweep voltammetry experiments were carried out in the phosphate solution described above with Au-Cu-Cd (2, 5, 10, 20, 50 mA/cm^2, ~60 μm) cathodes. Typical polarization curves are shown in Fig. 1-3. The peculiarities of the shape of each curve (waves and plateaus) can be interpreted in terms of the scheme proposed in Ref. 7 for the case of Au, Cu, and Au-Cu. We do not go into further mechanistic details here; rather, we are interested in relative effects

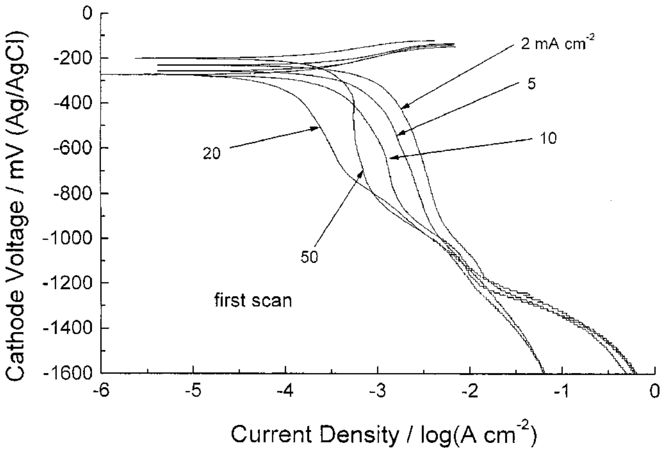

Figure 1. Linear sweep voltammograms for HER on Au-Cu-Cd alloys electrodeposited at various current densities. The curves were obtained at the first scan of a series of four successive scans.

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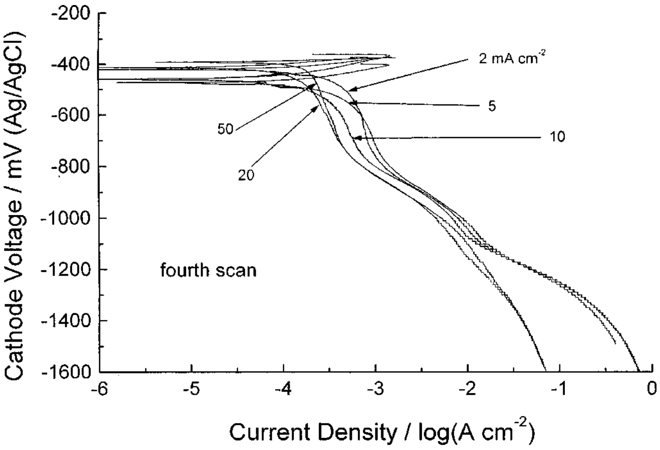

Figure 2. Linear sweep voltammograms for HER on Au-Cu-Cd alloys electrodeposited at various current densities. The curves were obtained at the last scan of a series of four successive scans.

brought about by the composition of the tested alloys and by the effects of HER. As far as limiting cds and wave potentials are concerned, approximately the same values were observed as those for Au-Cu alloys, and the same comments apply in this case. The most obvious plateau present in the polarization curves (−400 to −800 mV) is clearly affected by the composition of the cathode (Fig. 1 and 2). In addition, the shape of the curves changes with the number of successive scans (Fig. 1-3, particularly Fig. 3).

Observe in Fig. 1 that, except for the alloy grown at 50 mA cm^{-2}, there is an anticorrelation between plateau cd and electrodeposition cd, *i.e.*, Au content. This result indicates that the catalytic activity is higher for the alloys with higher Au content. This view is further confirmed by the high voltage quasi-Tafel slope, which is much higher for Cu-rich cathodes. The exception of the highest cd sample can be attributed to its much higher specific surface area resulting from unstable crystal growth at the current close to the limiting cd. Figure 3 indicates that the catalytic activity of high Au samples, as evaluated from the plateau cd, seems to be degraded by potentiodynamic cycling. This behavior is probably attributable to Au impoverishment of Au atoms at the surface as determined by EDS after the HER experiments. The high voltage quasi-Tafel behavior is unaffected.

Compositional effects of HER.—The results of compositional analyses performed by EDS of samples obtained at various cd values, before and after HER, are reported in Fig. 4. After the HER, the surfaces (EDS analyses are sensitive to the depth of ~2 μm in the relevant alloys) of Au-rich deposits tend to be slightly depleted of Au, while those of Cu-rich deposits tend to be rich in Au.

Morphological effects of HER.—The surface morphology of single phase Au-rich deposits (2 mA cm^{-2}, Fig. 5a) consists of a granular structure with sharp ridges, very similar to those observed

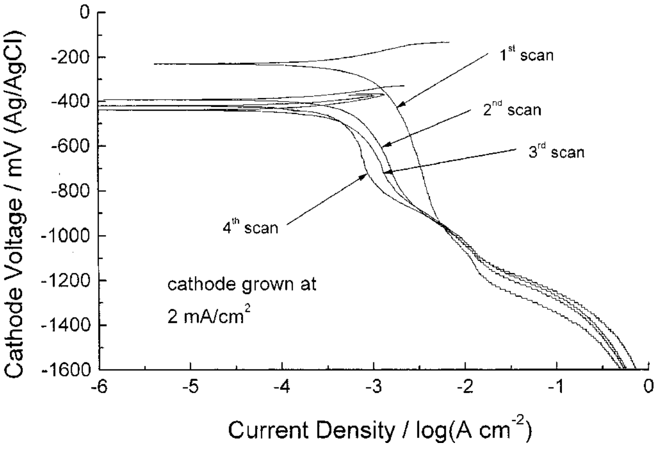

Figure 3. Linear sweep voltammograms for HER on an Au-Cu-Cd alloy electrodeposited at 2 mA cm^{-2} (highest Au content). The curves relate to a series of four successive scans.

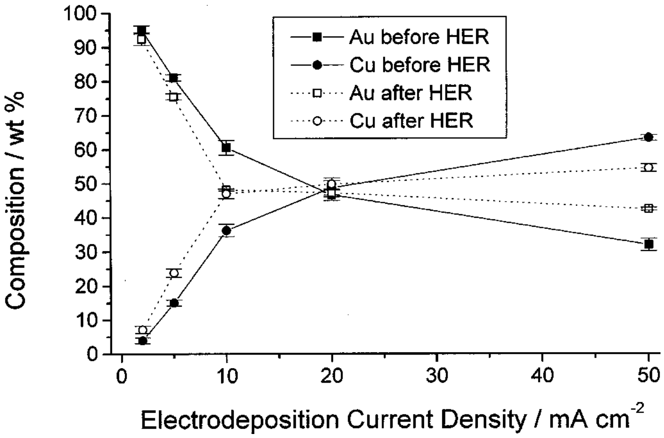

Figure 4. EDS compositional analyses of Au-Cu-Cd alloys electrodeposited at various current densities before and after HER (error bars refer to one sample standard deviation evaluated on four replicated analyses).

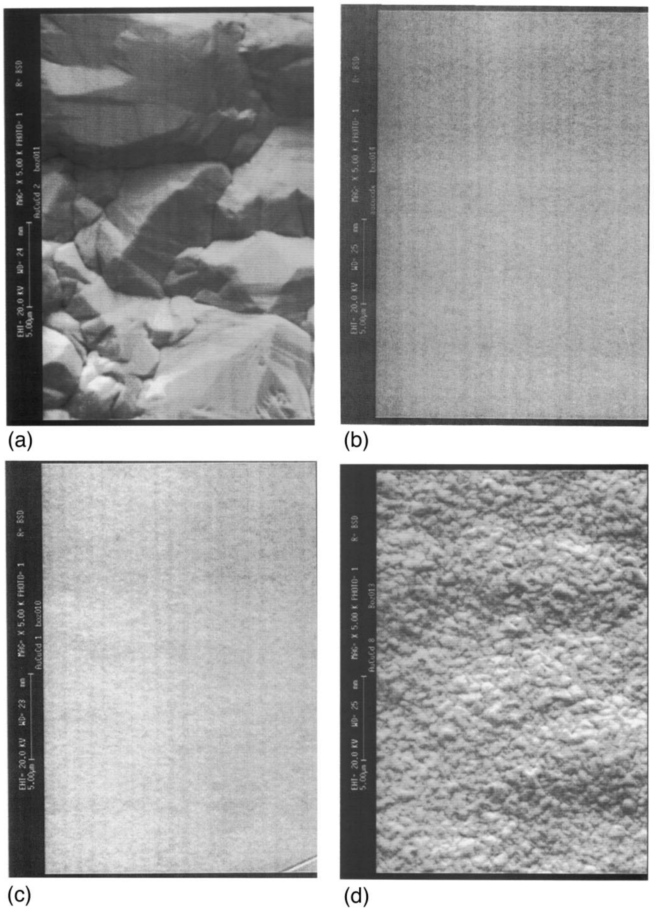

Figure 5. SEM micrographs of Au-Cu-Cd alloys electrodeposited at various current densities (mA cm^{-2}): (a) 2, (b) 5, (c) 10, (d) 20.

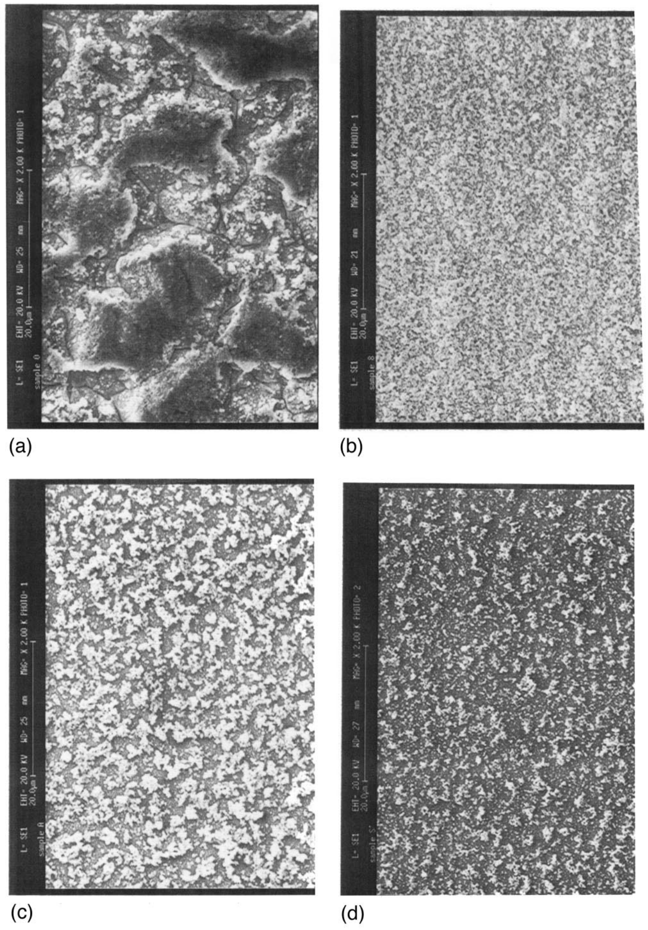

Figure 6. SEM micrographs of Au-Cu-Cd alloys electrodeposited at various current densities after HER, at electrodeposition current densities (mA cm^{-2}): (a) 2, (b) 5, (c) 10, (d) 20.

with Au-Cu alloys.[7] With larger amounts of codeposited Cu, a very smooth morphology is obtained (5 mA cm^{-2}, Fig. 5b), which tends first to develop a very slight waviness (10 mA cm^{-2}, Fig. 5c) and then to grow unstable through the formation of granular (20 mA cm^{-2}, Fig. 5d) and powdery features at the highest cd values investigated (50 mA cm^{-2}).

The SEM morphology is altered profoundly by HER. In general, a submicrometric granular structure appears on top of the as-plated morphology (Fig. 6). In particular, the large crystals of low Cu samples grown at 2 mA cm^{-2} are attacked and flattened (Fig. 6a) and this alteration correlates with the disruption of crystallographic preferred orientation, described in the subsection on structural effects of HER. Such an HER effect was not observed on high Cu samples grown at 50 mA cm^{-2}. This morphological alteration is seen even more clearly by AFM observation of smooth samples (10 mA cm^{-2}). Isolated submicrometer humps can be resolved by AFM in as-plated samples, protruding from a flat surface (Fig. 7). After HER, these humps are enlarged and take the shape of growth crystallites. The humps are no longer isolated, but occupy the entire surface of the cathode (Fig. 8).

SEM observations can be quantified by laser interferometric profilometry, which yielded the average roughness, R, and root mean square roughness, R_{rms}, data shown in Fig. 9. The averaging effects of HER can be observed.

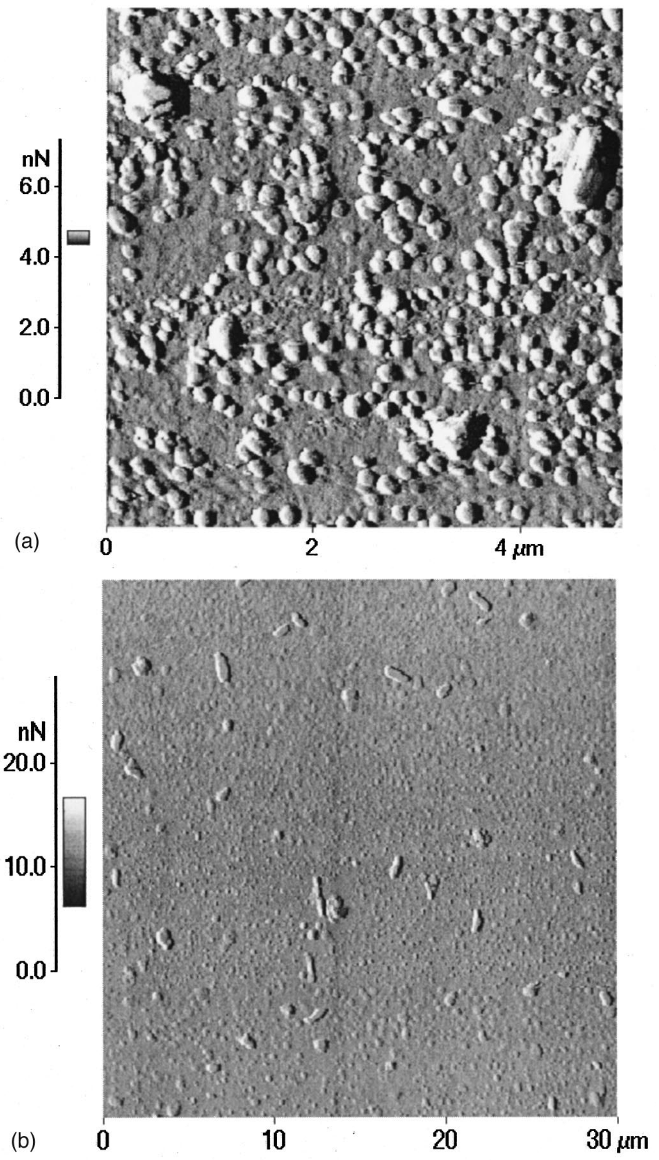

Figure 7. AFM images of a Au-Cu-Cd alloy electrodeposited at 10 mA cm^{-2}, as as-plated sample. Images at two different magnifications are shown in parts a and b.

Structural effects of HER.—XRD work was performed for the relevant alloys before (Fig. 10) and after (Fig. 11) HER. Highly (111)-ordered Au-rich phases are obtained at low cd values (2, 5 mA/cm^2). At 10 mA/cm^2, three highly (111)-oriented phases can be observed with different reticular parameters. In high Cu deposits (20, 50 mA/cm^2), two highly (111)-oriented, disordered face-centered cubic phases are obtained with the Cu-rich phase prevailing.

HER affects the XR crystallographic structure markedly. The (111)-PO of the as-plated deposits is disrupted. In addition, traces of a Cu-rich phase appear in high Au samples, while a Au-rich phase tends to separate in high Cu deposits, which is in agreement with the EDS data. It is worth noting that no sign of ordering is seen after HER.

LECO analyses.—LECO thermal desorption measurements of as-plated samples show that virtually no hydrogen is incorporated during the electrodeposition from the bath described in this paper. Spectra of cathodically charged alloys show that hydrogen is incorporated only in the low energy trap at 450°C.[7] This behavior is general for all the investigated Au-Cu-Cd alloys, irrespective of composition, structure, and morphology. Typical amounts of hydrogen incorporated under the above-described conditions are in the range of 0.3 to 0.7 mL g^{-1}.

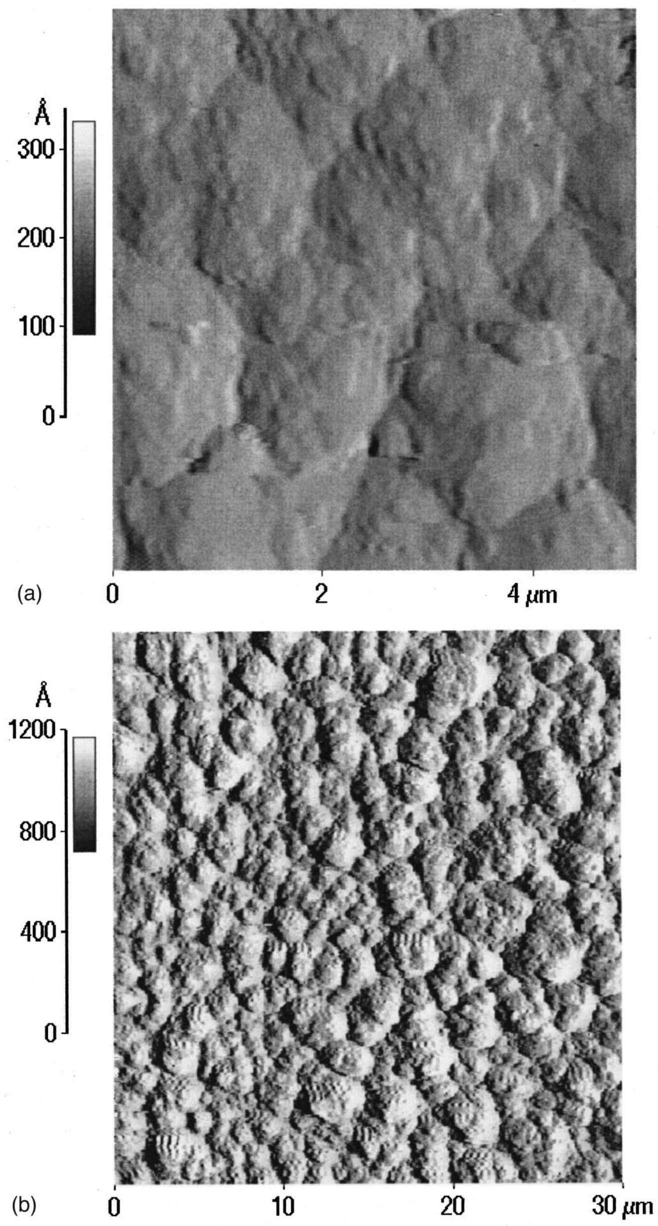

Figure 8. AFM images of a Au-Cu-Cd alloy electrodeposited at 10 mA cm^{-2}. The sample was subjected to HER. Images at two different magnifications are shown in parts a and b.

Conclusions

The electrode kinetics, as measured by linear sweep voltammetry of HER from a slightly acidic solution, is affected by alloy composition and scan repetition. A reduced electrocatalytic activity of Cu-rich alloys was observed. Subsequent scans gave rise to a relative reduction of catalytic activity. Prolonged galvanostatic HER gives rise to a series of alterations in Au-Cu-Cd cathodes with a range of compositions. The Au content of the alloys, as measured by EDS, is systematically reduced. As far as SEM surface morphology is concerned, the relatively large crystallites of Au-rich deposits are attacked and flattened; globular dispersed features grow on the flat surfaces of Cu-rich deposits. AFM reveals finer details of these morphological alterations for flat deposits: initially tiny and separated humps, which cannot be resolved by SEM, tend to grow and then collapse. The morphological evolution can be followed also with laser-interferometric rugosimetry, but the low lateral resolution of

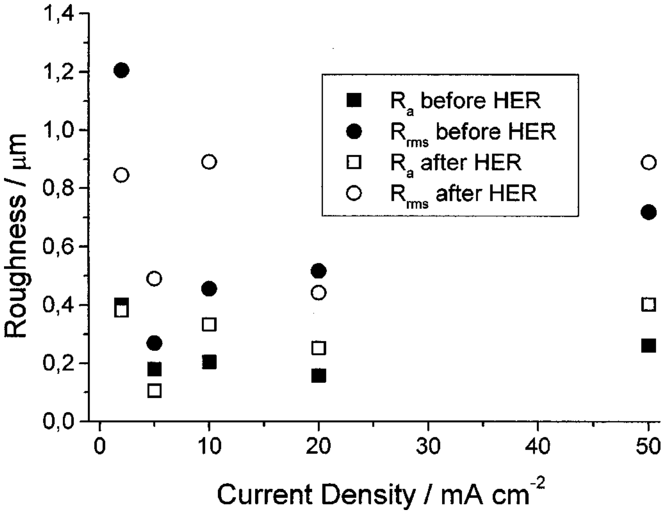

Figure 9. Laser interferometric measurements of R_aR_{rms} of Au-Cu-Cd alloy electrodeposited at various current densities before and after HER.

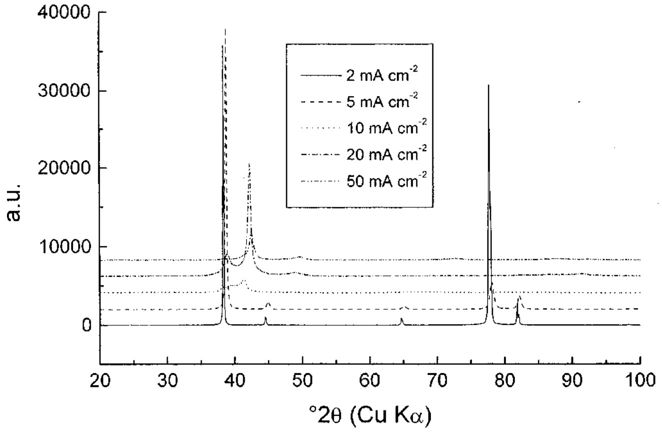

Figure 10. X-ray diffractograms of Au-Cu-Cd alloys as electrodeposited at various current densities.

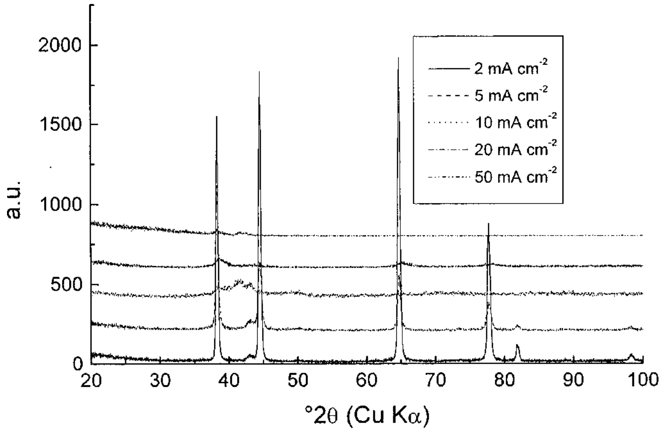

Figure 11. X-ray diffractograms of Au-Cu-Cd alloys electrodeposited at various current densities after HER.

the technique makes it sensitive only to the average aspects of the relevant variations. The crystal structure, as observed by XRD, is affected by prolonged HER: the originally (111)-preferentially oriented layers tend to become disoriented and the appearance of a new Cu-rich disordered solid solution is observed.

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