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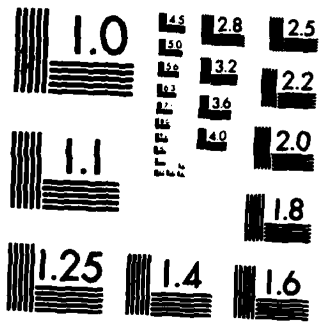


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In single-crystal electrochemical studies, various researchers have prepared the electrode surfaces by mechanical polishing followed by chemical polishing without further cleaning or high temperature annealing in vacuo. The quality of such single-crystal surfaces is in question. The present work has involved the use of LEED and Auger electron spectroscopy (AES) to examine the order and purity of the silver (111) and (100) surfaces after preparation with such procedures with the chemical polishing carried out in a cyanide-hydrogen peroxide solution. For both

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surfaces the LEED patterns have surprisingly well-defined spots indicating a high two-dimensional periodicity, although not as ordered as the UHV cleaned and annealed surfaces. Highly diffuse background and weak fractional-order spots are present in the LEED pattern of the chemically polished surfaces, probably due to random and ordered impurity adsorption during transfer to the vacuum chamber. The Auger electron spectra before sputtering indicate the main impurity to be carbonaceous with no nitrogen detected. Voltammetry curves in 0.1M HF in a thin-layer cell are generally featureless over the potential range -0.1 to +0.45V vs RHE. These data indicate that chemical polishing can yield silver single-crystal surfaces of sufficient quality to produce LEED patterns but still short of the quality for UHV cleaned and annealed surfaces.

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# STRUCTURE OF SILVER (100) AND (111) SINGLE-CRYSTAL SURFACES OBTAINED BY CHEMICAL POLISHING

by

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# STRUCTURE OF SILVER (100) AND (111) SINGLE-CRYSTAL SURFACES OBTAINED BY CHEMICAL POLISHING

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Key Words: LEED, silver single-crystals, chemical polishing.

Interest has been increasing in the investigation of electrochemical reactions on single-crystal electrode surfaces (see e.g. Ref. 1-7). Electrode processes having a pronounced dependence on the particular single-crystal surface include hydrogen adsorption (8-11), underpotential deposition of metals (4), oxidation of organic molecules (6) and oxygen reduction (7). Inadequately characterized single-crystal surfaces, however, may lead to misleading results. Atomically flat, well-ordered surfaces are needed in order to obtain meaningful data. Ultrahigh vacuum techniques such as low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) can facilitate the characterization of such surfaces and verification of freedom from adsorbed impurities, but these techniques are *ex situ*. Elaborate systems (8-11) have been developed for preparing and characterizing single-crystal electrode surfaces in ultra-high vacuum and then transfering them into the electrochemical environment and vise versa under conditions designed to minimize structural changes and contamination. Experiments with these transfer techniques, however, are very timeconsuming and impose substantial restraints on the types of electrochemical systems that can be studied because of factors such as the use of completely volatilizable electrolytic solutions and thin-layer cell configurations.

Some electrochemists, including one of the authors (RA), have prepared single-crystal surfaces of metals by chemical methods and then proceeded to examine the electrochemical properties of these surfaces. This work, however, has left unanswered the question of the quality of the single-crystal surfaces. This communication presents results which demonstrate that chemical polishing in the instance of silver single-crystal electrodes can yield ordered (100) and (111) surfaces, as judged by LEED.

Single-crystals of Ag, 99.99% pure, were obtained from Metal Crystals Ltd., Cambridge, England. They were oriented to better than $1^{o}$, mechanically polished by standard metallographic techniques with diamond paste, gradually decreasing the size of the grit to 1 micron. The crystals were further polished chemically, using procedures similar to those already reported (12). An aqueous solution of 30 volume percent of $H_2O_2$ and a solution of 21.5 g/l of NaCN were mixed in a 1:1 ratio for polishing the Ag(111) single-crystal surface. For the Ag(100) face, a lower concentration of 20 volume percent of $H_2O_2$ was used. The crystals were held for 5 s in these solutions, during which time vigorous gas evolution occured. They were taken out, held in air for 3 s and transfered into a solution of 37.5 g/l NaCN, where gas evolution ceased. After washing, the procedure was repeated several times, in most instances in a fresh solution of $H_2O_2$ and NaCN until a highly reflecting surface was obtained. The electrode surface was then thoroughly washed in pure water. The surface obtained in this way was protected by a drop of pure water and transfered into the UHV preparation chamber of the LEED-AES-XPS system, which has been described in prior publications (8,9). The water drop was then volatilized during the pump down.

Figure 1a shows the LEED pattern from the Ag(111) surface immediately after introduction into the UHV chamber at $10^{-10}$ Torr. This LEED pattern was obtained without cleaning the surface in the vacuum chamber in any way. Neither argon-ion sputtering nor thermal annealing was used. Figure 1b shows the LEED pattern of chemically polished Ag(111) after a single sputtering with an argon-ion gun (Varian model 981-2043) for three min at 1.5 kV and subsequent radiative thermal annealing at approx. 600°C. The crystal reached this temperature in approximately 5 minutes and was allowed to cool to room temperature, which required about 20 minutes in vacuum. Analogously, Figures 2a and 2b show LEED patterns of chemically polished Ag(100) before and after, respectively, UHV sputtering and annealing.

For both the (111) and (100) crystal faces before UHV sputter cleaning, highly diffuse background and weak fractional-order spots are present in the LEED pattern, probably due to random and ordered impurity adsorption during transfer to the vacuum chamber. Auger electron spectra before sputtering indicate the main impurity to be carbonaceous. No nitrogen was detected in the AES, indicating no substantial amount of $CN^-$ remained on the surface. The LEED spots are surprisingly well-defined, indicating a high two-dimensional periodicity, although not as ordered as the UHV cleaned and annealed surfaces. Voltammetry curves were also obtained in 0.1M HF in a thin-layer cell using a special transfer technique (8,9). Over the potential range -0.1 to 0.45V vs RHE voltammetry curves were generally featureless.

These data demonstrate that chemical polishing can yield silver single-crystal surfaces of high enough quality to produce LEED patterns. This is of great importance for studies of these surfaces outside UHV systems.

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## REFERENCES

1. "Surface Physics of Materials", Vol. I, J.M. Blakely, ed., Academic Press, N.Y. (1975).
2. G. Somorjai, "Principles of Surface Chemistry", Prentice-Hall Inc., Englewood Cliffs, N.J. (1972).
3. A. Hamelin, T. Vitanov, E. Sevastyanov and A. Popov, J. Electroanal. Chem. Interfacial Electrochem., 145, 225 (1983).
4. K. Juttner and J.W. Lorenz, Z. Phys. Chem., N.F., 122, 163 (1980).
5. R.R. Adzic, A.V. Tripkovic and W.E. O'Grady, Nature, 296, 137 (1982).
6. J. Clavilier, R. Parsons, R. Durand, C. Lamy and J.M. Leger, J. Electroanal. Chem. Interfacial Electrochem., 124, 321 (1981).
7. R.R. Adzic and N.M. Markovic, ibid., 138, 443 (1982).
8. A. Homa, E. Yeager and B.D. Cahan, J. Electroanal. Chem. Interfacial Electrochem., 150, 181 (1983).
9. A. Homa, Ph.D. Thesis, Case Western Reserve University (1981).
10. A.T. Hubbard, R.M. Ishikawa and J. Katekaru, J. Electroanal. Chem. Interfacial Electrochem., 86, 271 (1978).
11. P.N. Ross Jr., This Journal, 126, 1 (1979).

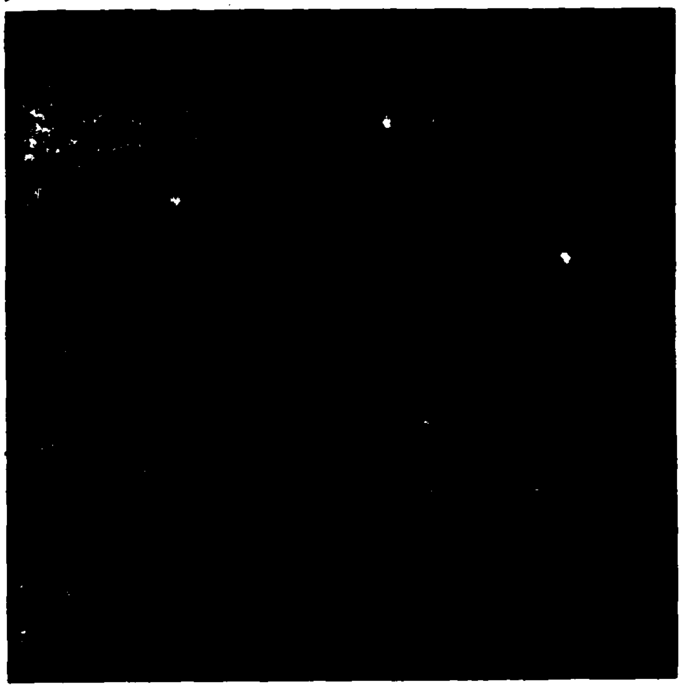

Figure 1a. LEED pattern of chemically polished Ag(111) immediately after introduction to the vacuum chamber (no sputtering or thermal annealing). Primary beam energy = 47 eV. Exposure time = 3 min. F-stop = 1.4, Kodak Panatomic X film for all exposures.

Figure 2a. LEED pattern of chemically polished Ag(100) immediately after introduction to the vacuum chamber (no sputtering or thermal annealing). Curvature of the pattern is due to the sample protruding inside the radius of the screen because of its unusually large size for the system. Primary beam energy = 48 eV. Exposure time = 3 min.

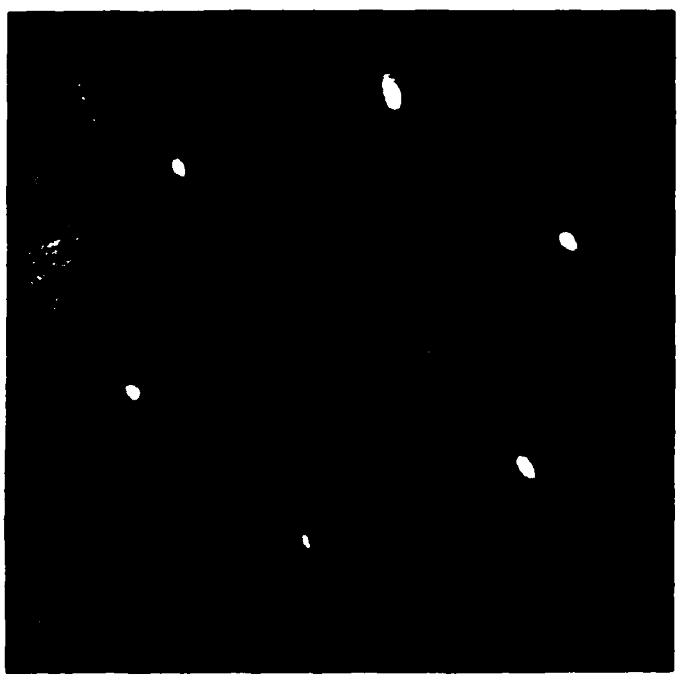

Figure 1b. Same as Figure 1a after sputtering at 1.5 kV for 3 min. and thermally annealing at 600°C. Primary beam energy = 45 eV. Exposure time = 30 s.

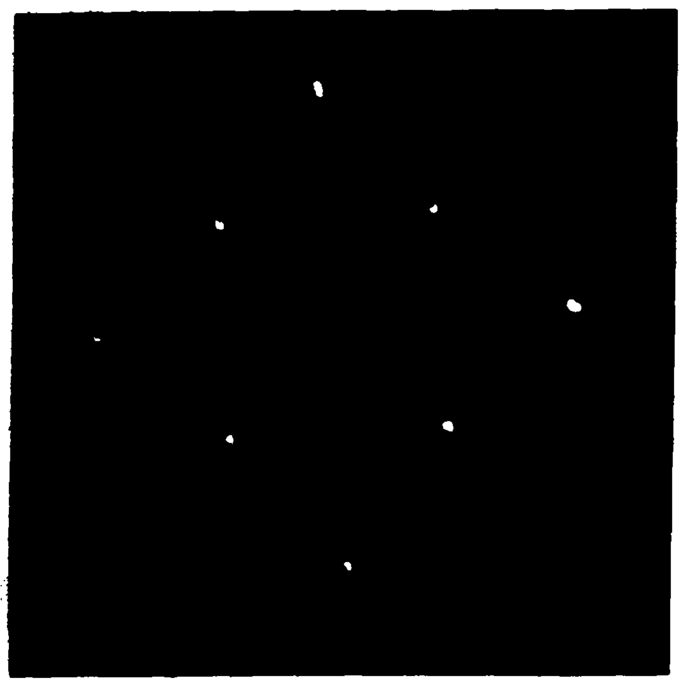

Figure 2b. Same as Figure 2a after sputtering at 1.5 kV for 3 min. and thermally annealing at 600°C. Primary beam energy = 60 eV. Exposure time = 30 s.

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