

STRUCTURE AND STABILITY OF THE (100) SURFACE OF GOLD

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Our continuing low-energy electron diffraction studies of gold surfaces have revealed patterns similar to the "domain" and "ring" patterns recently reported by Hagstrom, Lyon, and Somorjai¹ for (100) platinum surfaces. Although they attribute these structures to a clean surface, it should be noted (as they have done) that no other clean metal surface has been demonstrated to undergo rearrangement, and, moreover, that the theory of surface energetics² does not predict stable complex structures of the type observed on pure surfaces. Furthermore, reports of studies by Tucker³ of platinum of similar purity, in contrast, contain no discussion of the observation of such complex surface structures. In view of these facts, it is our present purpose to present the pertinent results of our gold studies and to propose a model in which the structures revealed by "domain"- and "ring"-type patterns are related to the presence of significant amounts of surface impurities.

We have observed weak diffraction patterns characteristic of a normal (1×1) bulk-type structure on electropolished (100) gold surfaces. As the crystals were heated, in vacuum, to successively higher temperatures, up to approximately 900°C, the corresponding diffraction patterns, observed after cooling to room temperature, decreased in intensity and finally completely disappeared while the intensity of the background increased. Glow-discharge ion bombardment in pure argon, of electropolished and annealed surfaces, resulted in the appearance of (1×1) patterns of increased intensity. As sputtering was continued, however, a (5×1) "domain"-type structure similar to that reported by Somorjai resulted. This pattern or structure was observed to degenerate in intensity with time at room temperature in the ultrahigh vacuum (uhv) environment. Finally, annealing at temperatures in the range ≈200°C to <800°C regenerated the "domain" structure.

The "domain" structure was observed at temperature to transform rapidly and reversibly to a normal or (1×1) structure at 806 ± 5°C. This transformation temperature re-

mained stable after extended annealing times at temperatures either above or below that required for transformation in either the uhv environment or 10⁻⁶ Torr of oxygen and hydrogen. Patterns subsequently observed on cooling to room temperature were found to be similar to, though always less well developed than, the "ring"-type patterns associated with platinum.¹ After such treatment, the "domain" pattern was most easily regenerated via additional ion bombardment and low-temperature annealing.

Samples examined after electropolishing and ion bombardment, without any intervening high-temperature treatment, behaved in a similar fashion. In both cases, short sputtering times seemed to encourage the development of strong (1×1)-type patterns while increased sputtering and/or annealing tended to result in generation of (5×1) "domain"-type patterns. In all instances the patterns associated with these structures were insensitive to environmental oxygen and hydrogen at room temperature while exposure for long times to the vacuum environment, as noted above, resulted in a general reduction in the intensity of the diffraction maxima and a simultaneous increase in the background intensity.

Our interpretation of the above observations is as follows: The (100) surface of an electropolished gold crystal consists of a thin, highly stable film of unidentified impurities which accumulate during the formation of an anodic film. Substantial rearrangement of these impurities occurs during annealing while significant desorption fails to take place even at temperatures approaching the melting point of gold. Most complete removal of these impurities is effected via either combined high-temperature desorption and ion bombardment or ion bombardment alone.

The impurity concentration obtained at the surface in these experiments rarely, if ever, approaches zero. Although ion bombardment, initially at least, is an effective means of reducing the concentration of surface-active impurities, whether they are introduced during electropolishing or through diffusion from the

bulk, continued removal of material results in an increased surface impurity concentration. This increase then results in the formation of the (5×1) "domain" structure which has been demonstrated to disorder reversibly at 806°C . A second, more stable configuration associated with the appearance of "ring"-type diffraction patterns follows extended high-temperature annealing. Ion bombardment of the "ring" structure results in either a redistribution of impurity or a change in its concentration. This change is accompanied by the regeneration of the "domain" structure. Finally, we believe that diffusion or adsorption processes which are operative at room temperature are responsible for the slow degradation of all the structures observed.

Contrary to the interpretation of Hagstrom, Lyon, and Somorjai¹ that the "ring"-type patterns are due to disordering of a clean surface, we believe that such patterns arise from a large number of small (in relation to the size of the electron beam) two-dimensional domains of an impurity phase. Each domain has the same projected symmetry parallel to the (100) gold surface, but there are rotational misorientations of the individual regions about the [001] axis.

Supporting our impurity-surface model are the results of Honig⁴ who demonstrated that anomalously high concentrations of bulk alkali metal and other impurities are ejected during ion bombardment of silver. Bradley⁵⁻⁷ has reported similar findings for platinum while Ruedl and Bradley^{8,9} have determined that the substantial surface concentration of sodium and potassium found by mass analysis of species ejected during sputtering of 99.999% copper, although undetected by conventional bulk analysis techniques, is increased during prolonged bombardment. The increase of surface impurity concentration is apparently due to selective sputtering. Furthermore, subsequent annealing was found to reduce the impu-

rity concentration only slightly.

In view of the findings of these investigators and our own results, we believe it is very probable that the "domain" and "ring" structures observed on gold (and platinum) are directly related to the presence of impurities. The observation of an invariant temperature for the reversible transformation of the complex (5×1) "domain" structure to a normal (1×1) bulk-type structure, it is felt, further justifies the surface-active impurity model. Alternatively, the theory of surface energetics¹⁰ predicts that, for a clean surface, rearrangement should occur in such a manner as to favor the stabilization of higher entropy (complex) structures above, rather than below, some critical temperature. Finally, surface-active impurities and selective sputtering mechanisms would seem to deserve increased attention in future studies of the preparation and determination of "pure" surface structures.

¹S. Hagstrom, H. B. Lyon, and G. A. Somorjai, *Phys. Rev. Letters* **15**, 491 (1965).

²J. K. MacKenzie, A. J. W. Moore, and J. F. Nicholas, *J. Phys. Chem. Solids* **23**, 185 (1962).

³C. W. Tucker, Jr., *J. Appl. Phys.* **35**, 1897 (1964).

⁴R. E. Honig, *J. Appl. Phys.* **29**, 549 (1958).

⁵R. C. Bradley, *J. Appl. Phys.* **30**, 1 (1959).

⁶R. C. Bradley, *Phys. Rev.* **117**, 1204 (1960).

⁷R. C. Bradley, A. Arking, and D. S. Beers, *J. Chem. Phys.* **33**, 764 (1960).

⁸E. Ruedl and R. C. Bradley, *J. Phys. Chem. Solids* **23**, 885 (1962).

⁹R. C. Bradley and E. Ruedl, *J. Appl. Phys.* **33**, 880 (1962).

¹⁰C. Herring, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer and C. S. Smith (University of Chicago Press, Chicago, 1953), p. 5; W. W. Mullins, *Metal Surfaces: Structures, Energetics, and Kinetics* (American Society for Metals, Metals Park, Ohio, 1963), P. G. Shewmon and W. M. Robertson, *Metal Surfaces: Structures, Energetics, and Kinetics* (American Society for Metals, Metals Park, Ohio, 1963), p. 67.