Letters

Influence of Surface Imperfections on the Epitaxy of Gold on Silver and the Coherence of a Carbon Film Deposited on Silver

Pashley, working on silver films evaporated on to cleaved mica substrates [1, 2], showed that good epitaxy occurs over a wide range of temperatures, but the orientation of the film depended as much on the substrate temperature as on the film thickness and the substrate orientation. Another important factor is the lattice misfit: in general terms, the less the difference between the lattice constants for the substrate and the film, the better the epitaxy produced. Nevertheless, Schulz [3] observed that oriented overgrowth can exist with a 27% lattice misfit for alkali halides condensed on to mica, and correlation of lattice misfit with epitaxy is now known to be subject to many exceptions. Epitaxy is also influenced by the surface topography of the substrate. Allpress and Sanders [4], studying surface structures, observed good orientation on atomically flat surfaces as well as on complex planes with a high concentration of kink atoms on them. Vermout and Dekeyser [5], investigating the influence of steps and other imperfections of the surface topography on epitaxy, made carbon replicas of newly-cleaved alkali halides and evaporated silver on to them, observing some measure of oriented overgrowth of the silver film on the replicas; specifically, these silver films showed "preferential orientation, . . . not extremely marked". In the present work, the growth of evaporated gold on to silver substrates at room temperature and on to carbon replicas of silver specimens has been studied in order to determine the importance of the various factors in the phenomenon.

The samples were $\{1\,1\,1\}$ single-crystal films of silver, and silver polycrystalline films, following the techniques described by Allpress and Sanders [4]. A group of specimens, single crystals as well as polycrystals, were thermally etched in air at 800° C, and the rest of them were left without any treatment. Several experiments were performed with the specimens, having the common characteristic that they were carried out at room temperature and under a pressure of 10×10^{-5} torr.

The first experiment consisted in evaporating gold directly on to the specimens. It was observed that excellent oriented overgrowth was produced for the gold films condensed on silver single crystals which had been thermally etched, on untreated single crystals, and on thermally etched polycrystalline films. Epitaxy was not observed on the polycrystalline silver films which had not been etched. (On polycrystalline films, epitaxy was assessed by selected area diffraction from individual substrate grains.)

In the second experiment, carbon replicas were made of all the samples. In all such experiments, replicas were turned around and gold was evaporated on to the "right side" of the replicas, the side which had been in contact with the silver. On condensing gold on to the replicas and observing the results, *no* epitaxy was detected in any instance.

In the third experiment, carbon replicas were made of freshly-cleaved rock-salt substrates, and silver was condensed on the right side of the replicas. The rock-salt substrates were warmed to 200° C *in vacuo* and then exposed to air, prior to the carbon deposition, following the technique described by Vermout and Dekeyser [5]. But in this case also, no epitaxy was observed on the replicas.

In the light of the results of the first experiment, the influence of the temperature at which gold was deposited will be considered. If the substrate is warmed, the mobility of the arriving atoms is increased, and oriented nucleation occurs better under these conditions. Nevertheless, in this case, where the experiments were carried out at room temperature, good oriented overgrowth was observed. So, the formation of oriented gold overgrowths on silver substrates is not appreciably impeded by the loss in the mobility of the arriving gold-atoms.

Secondly, in considering the geometry of the surface, two factors must be taken into account: one is the misfit of the lattice constants and the other is the surface topography of the substrate. As to the misfit between the lattice constants of gold and silver, this is only 0.2%, so oriented overgrowth is highly favoured. As to the surface topography, on surfaces of complex orientation (high Miller indices) the nucleation of gold is possible thanks to the high concentration of kink sites [4] at which gold-atoms are adsorbed, each forming six nearest-neighbour bonds with the silver-atoms, thus forming a coherent layer on the substrate. This is the case of the thermally etched silver polycrystalline films because thermal etching produces large flat areas of simple planes of the {111} and {100} type, bounded by curved complex facets rich in kink atoms, according to Allpress and Sanders [4]. On parts of the surfaces which are parallel to these simple planes, gold-atoms move freely on the substrate surface, until the surface supersaturation is high, and imperfectly oriented three-dimensional gold nuclei are formed. These planes also present monatomic steps due to emerging dislocations, which pierce the surface and where gold nucleates preferentially. This applies to the silver single crystals and to the simple planes in thermally etched silver polycrystalline films. As to the polycrystalline films without thermal etching, no epitaxy was observed. This may be because the grains are oriented at random and there are not exposed a sufficient number of complex oriented facets rich in kink sites (which only appear, together with simple planes, under a treatment such as the thermal etching). Nevertheless, one would have expected epitaxy on some of the grains of unetched polycrystalline silver, and this aspect will require further examination.

Working with replicas of the specimens, the influence of the misfit of the lattice constants was eliminated and so was the influence of the field of the kink atoms; only the influence of the geometry of steps and emerging dislocations [5] remain. As all the results, even the repetition of Vermout and Dekeyser's experiment, were negative, epitaxy (as distinct from the distribution of nuclei) is entirely influenced by the atomic field of the substrate, rather than by the geometry of surface defects.

Taking into account this last consideration, which implies that there must be a direct contact between substrate and the evaporated film for epitaxy to exist, a further experiment was carried out. Carbon was condensed on to {111} silver single crystals, with and without thermal etching, at room temperature and under a pressure of 10×10^{-5} torr. Gold was immediately evaporated on to the carbon film, under the same conditions. To separate the gold-carbon film from the silver substrate, the preparation was immersed in 50% HNO_3 and subsequently washed with distilled H_2O. The thickness of the carbon film was determined by extrapolation from the measured thickness of the film deposited on to a glass slide placed nearer the carbon electrodes. The thickness of this second carbon film was determined by Tolansky's method of multiple interferometry of a beam of monochromatic light. On observing the preparations in the electron microscope, epitaxy of the gold film was detected in the cases where the carbon film had an average thickness up to 10 Å and no epitaxy when the carbon thickness was higher than 10 Å.

The oriented overgrowth which appears when the carbon film is thinner than 10 Å is interpreted as due to the lack of coherence in the carbon layer, gold being able to grow epitaxially in the places where the carbon layer presents holes. When the intermediate carbon film is thicker than 10 Å, it is coherent and as there is no direct contact between gold and silver, gold grows at random and not epitaxially. Since under a carbon film of 10 Å the irregularities of the substrate surface must be preserved, this last experiment confirms the idea that the geometry of the surface defects does not influence epitaxy.

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