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MASTER

**SURFACE CHARACTERIZATION OF CATALYTICALLY
ACTIVE METAL, ALLOY, AND COMPOUND FILMS**

Progress Report

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ABSTRACT

Characterization of several catalytically active metal epitaxial systems was carried out. In addition to the (111) Ag/(001) Cu system reported on last year, TEM, RHEED, and AES studies were carried out on the (111) Pd/(111) Cu system. A few studies were also made on the (111) Pt/(111) Au system. Pd grows on (111) Cu by a monolayer growth mechanism with misfit dislocations at the interface. The thinnest Pd layers are highly strained in compression. As the overgrowth thickens, the strain decreases rapidly so that very little remains after 3 monoatomic layers have formed.

The Auger line profile from a strained Pd monolayer in intimate contact with a Cu substrate is different from what one gets from bulk Pd. This result suggests that a line profile analysis of the AES spectra from monolayer epitaxial films may be useful in determining the modified electronic structure that results from the Pd/Cu interaction. This work would have important applications in understanding the role of the substrate in supported catalysts.

All the results obtained so far were carried out with a UHV-RHEED system built 12 years ago. Because of the almost continuous useage of this system on the Pd/Cu studies, little time was available for studying other potentially useful systems, such as those involving Pt. For this reason and the recent availability of a LEED instrument, a new and more flexible stainless steel UHV system was constructed. This system is almost finished at the present time. It will allow the simultaneous investigation of two catalytic systems, giving our research project much needed flexibility.

EPITAXIAL CATALYTIC BILAYER SYSTEMS

A. (111) Pd on (111) Cu

We are presently completing our characterization studies on this system. At the present time we know that the epitaxial growth of Pd on (111) Cu at 25°C is similar to that of Au on (111) Cu. In the thinnest layers, Pd forms flat islands with irregular misfit dislocations at the Pd/Cu interface. This result agrees with calculations of the critical thickness h_c for misfit dislocation generation in this system of $0.9 \text{ } \overset{\circ}{\text{A}}$, which is about one third of a monolayer. See Appendix II. When an average two monoatomic layer of Pd has been deposited ($\sim 5 \text{ } \overset{\circ}{\text{A}}$), we know from TEM that the overgrowth is completely continuous because Type I coincidence lattice misfit dislocations completely cover the interface. See Appendix I. The monolayer growth mode persists beyond $5 \text{ } \overset{\circ}{\text{A}}$ up to at least $36 \text{ } \overset{\circ}{\text{A}}$, the thickest overgrowth examined. In these studies the overgrowth thickness was measured by a quartz crystal microbalance.

We have also recently initiated Auger electron spectroscopy (AES) studies on the Pd overgrowths. One of our aims here was to show that the AES intensities can be used to measure overgrowth thickness for the first one or two monolayers when monolayer growth occurs. In this thickness range the AES intensities of overgrowth and substrate materials should vary linearly with coverage up to the first completed monolayer. For the second monolayer a lower slope should be obtained. Three dimensional island growth, in contrast to monolayer growth, would not give linear changes in intensity.

Figure 1 shows our first correlation of AES intensities with the thickness measured by the quartz crystal microbalance. The thickness of a (111) monolayer of Pd is expected to be $a_{\text{Pd}}^0/\sqrt{3} = 2.25 \text{ } \overset{\circ}{\text{A}}$, assuming an unstrained lattice. That is, complete monolayer coverage should occur when the Pd thickness reaches $2.25 \text{ } \overset{\circ}{\text{A}}$. Apparently linear changes in intensity occur for at least the first two monolayers, confirming the TEM results, which also indicated monolayer

growth. Figure 1 also shows that the breaks in the linear slopes occur almost exactly at the expected values of $2.25 \text{ \AA}$ and $4.50 \text{ \AA}$ for the first and second complete monolayers. Exact agreement is not expected since there is a small geometrical factor involved in the thickness measurements using the quartz microbalance. The results of Figure 2 giving the strain in directions parallel to the plane of the overgrowth would also imply a strain perpendicular to the surface, at least for regions that are two or more monoatomic layers thick. Finally, no differences in sticking coefficient are expected for Pd deposited on the monocrystalline Cu substrate and Pd deposited simultaneously on the polycrystalline Cu on the quartz microbalance.

Another piece of information that can be deduced from Figure 1 is the fractional surface area of the growing monolayer in the two regions, i.e. between 0 and 1 monolayer and between 1 and 2 monolayers. The complement to this number in the first region would be the fraction of the copper substrate surface that is not covered with a Pd overgrowth. In principle therefore one has a means for correlating the real surface area with its catalytic activity in a particular reaction.

As mentioned above, we have also made elastic strain measurements on these Pd overgrowths as a function of thickness h . See Figure 2. These measurements show that the thinnest overgrowths tend to be compressed in the plane of the overgrowth towards the lattice parameter of the copper substrate. As the overgrowth thickens, the average strain decreases rapidly. It seems very plausible that catalytic activity will depend significantly on the strain in these overgrowths since the interatomic distance must affect the electronic structure of the Pd overgrowth.

While the AES experiments indicate monolayer growth occurs even for the first monolayer, TEM measurements suggest complete coverage doesn't occur until the film thickness reaches $4.5 - 5 \text{ \AA}$. In this range long, straight Type I

(Appendix I and II) coincidence misfit dislocations can be observed everywhere in the bilayer. See Figure 3. Below this thickness range, the misfit dislocations are irregular, Type II (Appendix I), and do not completely cover the interfacial region. See Figure 4. They appear to be concentrated in irregularly shaped regions which would normally be interpreted as an island overgrowth microstructure. The streaked RHEED pattern in Figure 5 indicates that the islands are extremely flat.

We are presently looking for an optimum overgrowth thickness range between 3.5 and 5 Å that will give us a more symmetrical island structure from which island edge length can be more easily determined. Nevertheless, if edge length is important in catalytic activity in this system, then it should show up in the 0 to ~4.5 Å thickness range as an enhanced activity resulting from the excessive edge length per island.

The AES measurements have also shown that the Auger line shape of the Pd overgrowths depends on thickness. This result is expected since the initial strained monolayer consists of atoms that are interacting strongly with the Cu substrate. For atoms in the second monolayer, the interaction with the substrate becomes a second order effect. Clearly these results suggest the possibility of determining the influence of a substrate on the electronic structure of the overgrowth, and therefore on the influence of a substrate on the overgrowth's catalytic activity. It has been suggested to us by Dr. Robert Rye of Sandia Laboratories in Albuquerque (at the December 1978 DOE Catalysis Conference in Germantown) that a careful analysis of the Pd line profile as a function of overgrowth thickness should yield the modified electronic structure arising from the interaction of the Pd monolayer with the Cu substrate.

B. (111) Pt on (111) Au

This system and the (111) Pt on (111) Cu system were the two originally proposed for catalysis studies. However, difficulties in evaporating Pt were encountered initially. As a result our major efforts were then directed towards using Pd, which is much easier to evaporate. In the meantime the problem of evaporating Pt was resolved. We can now evaporate Pt at low rates fairly easily. Because only one UHV system was available for epitaxy studies, we continued our work on Pd. However, a second UHV system is now almost complete, so that we plan to continue the Pt/Au and Pt/Cu studies shortly. Again we will be looking for room temperature epitaxial growth since at higher temperatures Pt and Au interdiffuse readily.

Approximate calculations for the critical thickness for misfit dislocation generation are $0.7 \text{ \AA}$ and $2.4 \text{ \AA}$ for Pt/Cu and Pt/Au respectively. Since a (111) monolayer of Pt is $2.3 \text{ \AA}$ "thick", only the Pt/Cu bilayer would be expected to have misfit dislocations at the monolayer interface. Pt on Au may be pseudomorphic at first so that misfit dislocations may form only when the second monolayer starts to grow. This result is important since misfit dislocations are used in TEM to delineate the flat islands of the overgrowth. Since the calculations are quite approximate, it is necessary to perform the experiments in order to determine what exactly occurs.

C. (111) Au on (111) Cu and (111) Cu on (111) Au

These systems may be useful for catalysis studies involving Cu_2O , which is a catalyst for the CO oxidation reaction. They have already been characterized and some of the work has been published.¹⁻³ Two final manuscripts are now being prepared and will be submitted for publication most likely in May, 1979.⁴

Briefly, the (111) Au/(111)Cu system is very similar to (111) Pd on (111) Cu. Misfit dislocations are present in the thinnest layers. Also the Au over-

growth becomes completely continuous at around $6 \text{ \AA}$. Cu grows on (111) Au by a Stranski-Krastanov mechanism, namely by the formation of one or two monolayers (with misfit dislocations) followed by strain-free nucleation of three dimensional Cu islands on top of the initial monolayers. Both systems have interesting possibilities for catalysis involving Cu and the formation of Cu_2O during the reaction.

D. (111) Ag on (111) Cu, (111) Cu on (111) Ag, (111) Ag on (001) Cu

Ag is a catalyst for the oxidation of ethylene to ethylene oxide. This reaction is extremely important in the manufacture of plastics. The above three systems were characterized in our laboratory and the results published for (111) Ag/(111) Cu^{1,5} and (111) Cu/(111) Ag⁶. The results of the (111) Ag/(001) Cu system are in press.⁷ These systems should be very useful in studying the dependence of this very important reaction on surface microstructure, topography, and composition.

MAJOR NEW EQUIPMENT

A new stainless steel bell jar type of system is nearing completion. Originally it was planned that this system would take the place of our old UHV-RHEED system constructed in 1966-67.⁸ At present we plan to continue using the old system as long as we can because it adds considerable flexibility to our research program. In particular it allows experiments to be carried out simultaneously on two different catalytic systems.

The stainless steel bell jar for the new system was purchased on funds supplied in the first contract year. A new 110 l/s triode Vacion pump together with one new and one old sorption pump are used on the new system. However, we still need a titanium sorption pump to increase the pumping speed for reactive gases.

During the past year we have also tested the new Physical Electronics 5 Kev Auger electron spectroscopy system and repaired a ten year old Varian quadrupole mass spectrometer that hadn't worked for almost that long and which Varian wouldn't repair. Fortunately one of our post-doctoral fellows, Dr. E. A. Knabbe, has had a great deal of experience with such instruments and was able to make it work by correcting what was apparently a design error in the safety circuits. This mass spectrometer has only a Faraday cage and no electron multiplier. Thus its sensitivity is limited. However, we have used it to do some preliminary studies of the catalytic oxidation of CO to CO₂ on Pd films at 25°C.

Our plans are to use this old quadrupole on the UHV-RHEED system and put the new UTI quadrupole mass spectrometer (on order) on the new system. Thus the new system will be the main unit for catalysis studies while the UHV-RHEED system will be used for supplementary characterization investigations.

Another reason for building a second system was the recent availability of a Varian LEED system arising from the resignation of one of our faculty

members in Materials Science. Thus the new system will initially be a LEED-AES system, but we plan to add RHEED to it also. RHEED has some advantages over LEED in that the former can be used to study polycrystalline samples as well as monocrystals. LEED will only detect the monocrystalline regions of a sample while RHEED will give information on both if both are present. Also we plan to look at the Auger spectra developed from the higher energy (25-30 Kv) RHEED beam striking a smooth surface and compare it with that from the internal 5 Kv gun of the cylindrical mirror analyzer (CMA), which strikes the specimen at normal incidence. The RHEED beam, however, can be directed along arbitrarily selected crystallographic directions in the plane of the film (the RHEED beam strikes the surface at grazing incidence). Thus it appears that the information on electronic structure that is obtainable from the two techniques might be different and therefore complement each other.

The last major advantage of the new more flexible bell jar system is that it allows us to carry out directed or chopped beam experiments. It is felt that the high residual background of CO and CO₂ in the vacuum system may mask the catalytic effects that we will be looking for. In any case directed or chopped beam techniques will greatly increase the sensitivity of the proposed measurements. The old UHV-RHEED system just didn't have enough ports in the right places for such experiments.

PERSONNEL

Dr. Richard W. Vook, Professor of Materials Science, acted as Principal Investigator on this project. He is spending approximately 25% of his time during the current academic year on this project and expects to spend at least 1.5 months during the 3.5 month long summer on the project. Dr. Vook was assisted by Mr. Benjamin Chao, a full time graduate research assistant and Ph.D. candidate in Materials Science.

In addition two post-doctoral fellows, Dr. Ernst-Axel Knabbe and Dr. Bhoj Singh, each worked 50% of their time on this project. Dr. Singh obtained his Ph.D. in Physics from Keele University in England in 1971. He is presently on leave from the University of Jodhpur in India where he is a Lecturer in Physics. Dr. Singh is the author of twelve papers, mostly in the area of gaseous adsorption on thin films. Dr. Knabbe obtained his Ph.D. in Physics in 1978 from the University of Hamburg in Germany. He has published two papers in the area of atomic beam scattering experiments from thin films. Dr. Singh is expected to remain on the project throughout the proposed 1979-80 contract year. Dr. Knabbe may return to Germany in February of 1980.

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FIGURE 1: Auger intensity (in atomic %) of (111) Pd overgrowths on (111) Cu as a function of overgrowth thickness. Pd deposited at 25°C.

FIGURE 2: Lattice parameter of epitaxial (111) Pd overgrowths on (111) Cu. Monolayer growth mode. Pd deposited at 25°C.

FIGURE 3: Type I misfit dislocations in an epitaxial 5 Å (111) Pd overgrowth deposited on (111) Cu at 25°C.

FIGURE 4: Irregular Type II misfit dislocations in a 3.0 Å thick Pd overgrowth deposited on (111) Cu at 25°C.

FIGURE 5: RHEED from a 4 Å thick (111) Pd overgrowth formed on (111) Cu at 25°C. The Cu reflections are extremely weak.

Pd, Cu VS Pd THICKNESS

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5