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

MASTER

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Progress Report
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SUMMARY

The major achievements of the past year are listed in the appendices as papers accepted for publication. The work consists primarily of verification and confirmation of the Auger electron spectroscopy R-factor effect discovered by our research group approximately two years ago. The R-factor is a very sensitive measure of doublet Auger line shape changes or relative doublet line shifts. In applying it to the characterization of epitaxial layer growth, we have found that it can be used to identify epitaxial growth (in contrast to polycrystalline growth) and layer growth (in contrast to island or three dimensional growth). In these cases the R-factor oscillates periodically with added film thickness, for both thin and thick (≈ 1500 Å) films. The period equals the layer thickness. Since maxima in R are associated with a smooth surface and minima with a maximum in step density, R gives a measure of surface topography. This result is the first time that Auger electron spectroscopy has been applied to studies of surface topographic effects.

In addition an effect due to the substrate induced misfit strains on the Auger R-factor has been established. In the case of Pd on Cu and Ag on Cu, the Pd and Ag overgrowths are initially compressed towards the lattice parameter of the Cu substrate. As a result, the electronic energy levels in the overgrowths are expected to be spread farther apart, resulting in better resolved Auger doublets and a higher R-factor. In principle therefore, the R-factor can be used as a measure of lattice strain. These studies were carried out on (111)Pd/(111)Cu, (111)Ag/(111)Cu, (111)Cu, and (111)Ag surfaces to establish the general validity of the results initially obtained with Pd. It is clear that the use of Auger electron spectroscopy for characterizing surfaces has been significantly enhanced by these studies on thin films. The implications for chemisorption and catalysis

surface studies are apparent. Since the start of calendar year 1981 we have concentrated on experiments designed to determine the effect of steps (as characterized by the R-factor) on the chemisorption of oxygen on Pd. These studies are presently in progress.

I. REPORT

A. Research Results

The work carried out during the preceding year is reported in the Appendices to this Report. In these published or soon to be published papers we have established two basic R-factor effects. The first arises from the periodic nature of epitaxial layer growth and results in a corresponding thickness periodicity in R. It can be used to establish the presence of (a) epitaxy, (b) layer growth, and (c) a thickness periodicity in step density on the surface during layer growth. The second R-factor effect arises from the compressive strain induced in Pd and Ag films grown epitaxially on Cu. Such strains would spread the electronic energy levels in the overgrowth film and thereby induce improved Auger line resolution in close doublets, resulting in higher values for R. Thus strain effects can also be detected by Auger spectrometry.

We are presently carrying out oxygen chemisorption studies on these Pd films. It is expected that we will be able to adsorb oxygen at two distinctly different sites on the surface in a distinguishable manner. These two sites are step sites and flat surface sites. By varying the oxygen partial pressure (and possibly also the substrate temperature) along with the H_2 and CO residual gas background, it should be possible to chemisorb oxygen only at step sites where the binding energy should be higher than on the flat surface. Thus chemical reactions which take place preferentially on the flat areas (or alternatively at steps) should be capable of being distinguished from each other.

Figure 1 shows some very preliminary results on the adsorption of oxygen on (111)Pd surfaces as a function of added Pd film thickness. The ordinate is a measure of the amount of oxygen adsorbed. Clearly both the amount of oxygen and the amount of Pd oscillate with thickness. Also the O/Pd ratio oscillates. These

Figure 1: Auger Amplitudes vs Added Pd Film Thickness in a (111)Pd/(111)Cu Bilayer.

results are interpreted as indicating that oxygen is adsorbed almost entirely at surface steps, the density of which oscillates periodically with the (111) layer thickness. It is believed that oxygen which was incident on the flat areas of the Pd film was immediately desorbed by catalytic reaction with residual H_2 and/or CO to form H_2O or CO_2 . The residual hydrogen and carbon monoxide gases were produced by the ion pump and by outgassing from the walls of the stainless steel vacuum system.

It appears that when we start carrying out surface catalytic reactions we will be able to distinguish those reactions which occur on the flat surfaces from those that occur at steps. In these experiments we need only vary the step density on the surface by depositing more or less of the film material. The prospects are exciting for catalysis research.

B. Equipment Improvements and Modifications

We are presently using two UHV systems on this research. One is a new UHV system completed approximately 1 1/2 years ago having an Auger electron spectrometer, a quadrupole mass spectrometer and various other accessories. This system is used for all our AES studies, and mainly for the Pd/Cu work. The second system is our old UHV-RHEED system which has recently been renovated with a new Vac Ion 60 l/s pump and a new substrate holder mechanism for doing RHEED in a much faster and simpler way. Also the capability of forming 4 films of different substrates was introduced. This system is being used mainly for characterizing (111)Pt/(111)Au bilayers. AES measurements, however, will be carried out in the new UHV system described above.

C. Personnel and Activities

Dr. Richard W. Vook, Professor of Materials Science, acted as Principal Investigator on the project. He was assisted by Mr. Benjamin Chao, Mr. Pankaj Dixit, Mr. Bruno De Cooman, all full time graduate research assistants in Materials Sci-

ence. Mr. Chao left the project in September of 1980 to accept a position with Energy Conversion Devices. He has just recently turned in the first draft of his PhD Dissertation. Mr. Bruno De Cooman joined the project in January of 1981. Syracuse University paid his research assistantship for the Spring 1981 semester and it is expected that they will again do it in the fall of 1981. Mr. De Cooman is working on an M.S. in Materials Science.

Dr. Yoshikatsu Namba, Professor of Electrical Engineering at Tokyo Noko University, worked on the project until February 1, 1981. An offer of a post doctoral fellowship was made to his replacement in December of 1980, and it was accepted. Unfortunately one delay in arrival led to another, the final one being permanent. The prospective candidate became ill with a lung infection and couldn't start work at all. It is expected that his replacement will be chosen shortly.

Some of Dr. Vook's activities during the past year include a 6 week stay last summer at Dr. Carlos Colmenares' Laboratory at the University of California's Lawrence Livermore Laboratory. His work there involved two projects. One was an investigation of electron induced luminescence (EIL) from clean and selectively contaminated thorium surfaces. Luminescence spectra for electron irradiations in the presence of O_2 , CO , and H_2 were obtained. In addition a vacuum system was set up for forming epitaxial uranium films and studying their surfaces by LEED and AES. The aim of this work is to investigate corrosion phenomena on uranium crystal faces. Since single crystals of uranium are very difficult to obtain, the epitaxial technique looks very promising.

Dr. Vook is also cooperating with Drs. Jack Houston and Robert Rye at Sandia National Laboratories in Albuquerque, New Mexico. Computer tapes containing the Pd Auger line profiles were sent to this group. They plan to deconvolute the lines for us to get the true Auger line functions. Hopefully, they can then be analyzed to find out what in the line shape is changing when the Pd films grow epitaxially

on Cu. We plan to develop this capability ourselves sometime in the near future.

Finally, Dr. Vook has been invited to give a presentation at the Fifth International Thin Film Congress in Israel in September. This conference is usually attended by approximately 1000 scientists and engineers from all over the world. There are 16 technical sessions. Dr. Vook will be the invited speaker in the "Thin Films Characterization" session. He will speak on his DOE supported research.

II. PUBLICATIONS OF DOE SUPPORTED RESEARCH 1977 - Present

1. Vook, R. W., and Chao, S. S., "Misfit Dislocations in (111)Ag/(001)Cu Epitaxial Layers." *Thin Solid Films* 58, 203 (1979).
2. Vook, R. W., "Epitaxy and Misfit Dislocations in Large Misfit Systems," *Thin Solid Films* 64, 91 (1979).
3. Chao, S. S., and Vook, R. W., "Misfit Dislocations in (111)Pd/(111)Cu Bilayers." 37th Ann. Proc. Electron Microscopy Soc. Amer., San Antonio, Texas (1979), E. W. Baily (ed.) p. 464.
4. Macur, J. E., and Vook, R. W., "Initial Epitaxial Growth of (111)Au/(111)Cu and (111)Cu/(111)Au," *Thin Solid Films* 66, 371 (1980)
5. Macur, J. E., and Vook, R. W., "Interdiffusion Phenomena in Au/Cu and Cu/Au Bilayers," *Thin Solid Films* 66, 311 (1980).
6. Chao, S. S., Knabbe, E.-A., and Vook, R. W., "Auger Line Shape Changes in Epitaxial (111)Pd/(111)Cu Films." *Surface Science* 100, 581(1980).
7. Chao, S. S., Vook, R. W., and Namba, Y., "Thickness Periodicity in the Auger Line Shapes From EPITAXIAL (111)Pd/(111)Cu Films. *Journal of Vacuum Science and Technology*.
8. Namba, Y., and Vook, R. W., "Auger Analysis of Thick Ag Films and Ag Layers Grown on Cu". Accepted for publication in *Thin Solid Films*.
9. Namba, Y., Vook, R. W., and Chao, S. S., "Thickness Periodicity in the Auger Line Shape From Epitaxial (111)Cu Films." Accepted for publication on *Surface Science*.

III. LECTURES, SEMINARS, PRESENTATIONS FOCUSSED ON DOE SUPPORTED RESEARCH

A. Invited

1. Dec. 13-15, 1978 Heterogeneous Catalysis Research, U.S. Department of Energy, Germantown, Md., "Surface Characterization of Catalytically Active Metal, Alloy, and Compound Films." R.W. Vook.
2. April 20, 1979 Surface Science Seminar, University of California, Lawrence Livermore Laboratory, Livermore, California. "Epitaxial Growth in Large Misfit Systems."
3. April 26, 1979 Sixth International Conference on Metallurgical Coatings, San Diego, California. "Epitaxy and Misfit Dislocations in Large Misfit Systems."
4. July 10, 1979 Solid State Seminar, Xerox Corporation, Palo Alto Research Center, Palo Alto, California. "The Initial Stages of Epitaxial Growth in Large Misfit Systems."
5. July 31, 1979 Surface Science Seminar, Sandia Corporation, Albuquerque, New Mexico, "The Initial Stages of Epitaxial Growth in Large Misfit Systems and Their Relation to Catalysis."
6. Sept. 27, 1979 Materials Science Seminar, Cornell University, Ithaca, NY. "Initial Stages of Epitaxial Growth in Large Misfit Systems."
- *7. June 26, 1980 Rocky Mountain Chapter, American Vacuum Society, Aspen, Colorado. "Nucleation and Growth of Thin Films."
- *8. June 30-
July 3, 1980 DOE-SERI Workshop on Basic Research Needs and Opportunities in Interfaces in Solar Materials, Denver, Colorado.
9. August 14, 1980 General Chemistry Division Surface Science Seminar, University of California, Lawrence Livermore National Laboratory. "Thickness Periodicities in Auger Lines From Epitaxial Metal Films."
10. Jan. 6, 1981 Winter Conference on Surfaces by the National University of Mexico, the National Polytechnic Institute, and the Mexican National Petroleum Company in Cocoyoc, Morelos, Mexico. "Application of Auger Electron Spectroscopy to Epitaxial Growth."

*Dr. Vook was invited to these meetings but did not attend because of an auto accident he incurred while driving to Colorado.

11. Feb. 16-25, 1981 Six hours of lectures in the Physics Department of the Indian Institute of Technology in New Delhi on the "Structure and Growth of Thin Films." Visit sponsored by the NSF-CSIR, U.S.-India Exchange of Scientists Program.
12. April 7, 1981 Physics Department Condensed Matter Seminar, Syracuse University, "The Application of AES, RHEED, and TEM to Epitaxial Growth." R. W. Vook.
13. April 29, 1981 Syracuse University Institute for Energy Research Seminar. "Surface Preparation and Characterization-The Key to Understanding Catalysis and Corrosion Phenomena." R. W. Vook.
14. May 11, 1981 Surface Science Seminar, Sandia Corporation, Albuquerque, New Mexico, "Auger Measurements: A New Tool to Study the Growth and Topography of Epitaxial Thin Films."
15. Sept. 14-18, 1981 Fifth International Conference on Thin Films, Herzlia-on-Sea, Israel. "Characterization of Epitaxial Thin Films by RHEED, TEM, and AES." R. W. Vook.

III. LECTURES, SEMINARS, PRESENTATIONS ETC. (Con't)

B. Contributed

1. Fourth International Thin Film Conference, Loughborough University, Loughborough, England. "Misfit Dislocations in (111)Ag/(111)Cu Epitaxial Layers," R. W. Vook and S. S. Chao, September 11-15, 1978.
2. Electron Microscope Society of America Meeting, San Antonio, Texas, "Misfit Dislocations in (111)Pd/(111)Cu Bilayers", S. S. Chao and R. W. Vook, August 15, 1979.
3. 109th Annual Meeting of the Metallurgical Society of AIME, Las Vegas, Nev., "Catalytic Epitaxial Pd Films." R.W. Vook, S. S. Chao, E.-A Knabbe, and B. Singh. February 24-28, 1980.
4. 8th International Vacuum Congress, Cannes, France. "Initial Epitaxy of (111)Pt on (111)Au." E.-A. Knabbe, S. S. Chao, and R.W. Vook September 22-26, 1980.
5. 8th International Vacuum Congress, Cannes, France. "Epitaxial (111)Pd Films Formed on (111)Cu". S. S. Chao, R. W. Vook, and E.-A. Knabbe. September 22-26, 1980.
6. American Vacuum Society Symposium, Detroit, Michigan. "Auger Line Shape Changes in Epitaxial (111) Pd/(111)Cu Films." S. S. Chao, E.-A. Knabbe, and R. W. Vook. October 13-16, 1980.
7. Second International Conference on Solid Films and Surfaces. "Auger Line Shape Analyses for Epitaxial Growth in the Cu/Cu, Ag/Ag, and Ag/Cu Systems." R. W. Vook and Y. Namba, June 8-11, 1981.

IV. SYRACUSE UNIVERSITY COST-SHARING CONTRIBUTIONS

Year	RWV Salary Contribution	Fringe Benefit and overhead Contributions	Equipment and Cost	Miscellaneous Contributions	Total SU Contributions	Total DOE	Total Project	% From DOE
9/1/77- 8/31/78	\$1325	\$4908	Specimen Manipulator: \$2450	-----	\$ 8,683	\$ 80,000	\$ 88,683	90
9/1/78- 8/31/79	\$1350	\$4899	Vacuum pump & desk top computer: \$10,286	-----	\$16,535	\$ 83,400	\$ 99,935	83
9/1/79 12/31/80	—	\$10,020	Specimen Manipulator: \$3300 UHV Gate valve: \$2180	Subsidy, \$4000 (95% salary)	\$19,500	\$106,900	\$126,400	85
1/1/81- 12/31/81	—	\$8142	—	\$2428 Mr. Cooman's assistantship 1 semester	\$10,570	\$91,500	\$102,070	90