THEORETICAL AND EXPERIMENTAL INVESTIGATION OF THE PHYSICS OF CRYSTALLINE SURFACES

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I. The relation between the structure of epitaxial films and surface and interfacial energies (A. K. Green and E. Bauer)

The study of the growth of gold on sodium chloride has been continued during this report period. A major goal has been to understand the apparent discrepancy concerning the relative particle density on air- and vacuum-cleaved surfaces that was reported last period. All previously published data (including our own work) indicated that the particle density was always higher on the air-cleaved surface than on a vacuum-cleaved surface ($Na > N_V$). However, several of our recent experiments produced the result that $N_V > Na$. These experiments were performed with a new specimen holder and a slightly different geometry.

A complicating factor in comparing particle density is the step structure of the surfaces. The step structure is revealed by the preferred nucleation of gold particles on steps, i.e., decoration. Meaningful quantitative comparisons are only possible when large step-free regions are available for counting.

We have obtained the following results pertinent to this problem:

1. The particle density and step structure on air-cleaved surfaces are very sensitive to humidity exposure. Reproducible air-cleaved surfaces can be obtained by controlled exposures to known humidities.
2. The step structure on vacuum-cleaved surfaces varies from a close spaced linear structure to the elementary cleavage structure described by Bethge.[1]
3. The particle density on vacuum-cleaved surfaces is highly rate dependent on both steps and flat surface.
4. The particle density on air-cleaved surfaces is not rate dependent over the range we have investigated (0.1 to 1 Å/sec).

These results clearly show that the relative particle number on air- and vacuum-cleaved surfaces can vary considerably. A reliable statement of the particle number must include the following parameters: deposition rate, step structure of a vacuum-cleaved surface, and humidity exposure of an air-cleaved surface.

Result #2 has initiated an attempt to determine what parameters are decisive in obtaining relatively step-free surfaces. The initial experiments are to determine the influence of specimen temperature during the cleavage process. Preliminary results over a narrow temperature region (100°C - 250°C) indicate that temperature is unimportant. Further experiments over a wider temperature range are planned. Various pretreatments such as annealing, irradiating and stressing are being considered.

A recent publication[2] has claimed a strong influence of F-centers on the epitaxy of gold on sodium chloride.* We have repeated their experiment as closely as possible with a negative result. Because of the importance of this contradiction more work is planned to try and understand this discrepancy.

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*This would support the model of the effect of irradiation on epitaxy proposed by Rhodin, et al.[3] which is in contradiction to our model in which free alkali is made responsible for the irradiation effect.

REFERENCES

1. H. Bethge, phys. stat. sol. 2, 775 (1962).

2. T. Inuzuka and R. Ueda, Appl. Phys. Letters 13, 3 (1968).

3. T. N. Rhodin, P. W. Palmberg and C. J. Todd (to be published in Molecular Processes on Solid Surfaces, edited by E. Drauglis and R. Gretz, McGraw-Hill, New York, 1968).

II. Quantitative studies of the elastic and inelastic interactions of slow electrons with W single crystal surfaces (J. O. Porteus)

Investigation of the diffraction of plasmon-scattered electrons at low energies was extended during this report period to W(110) with 1/2 monolayer oxygen coverage, i.e., W(110) - O[1/2]. Diffraction by this surface should be quite sensitive to the penetration depth at which inelastic scattering occurs, and should thus provide basic information on the relationship of inelastic to elastic scattering in the crystal.

The low intensities and complexities encountered in this study necessitated some improvements in instrumentation and data acquisition procedure. These include increased stabilization and isolation of critical electronics, simpler manual beam alignment controls, a provision for semiautomatic point-by-point tracking of loss beams, and a better method of mapping these beams. A computer-compatible digital recording device for energy loss distributions, which will provide more accurate values of loss energies and inelastic intensities, is under development.

Loss beam mapping measurements have been made at normal incidence in the azimuth containing the 1/2,3/2 oxygen elastic beam. At secondary energies from 30 to 120 eV loss beam maxima are observed which substantially correspond to maxima in the elastic intensity vs. energy curve, as previously reported for clean W(110). However, unlike the case of clean tungsten, additional significant loss maxima are found at intermediate positions, especially near the upper end of the energy range. Such loss maxima are also found in the 1/2,3/2 azimuth of a clean W(110) surface at roughly the same positions in the colatitude angle vs. secondary energy plot.

These are tentatively identified as Bragg-case Kikuchi lines associated with the 11 reciprocal lattice rod. However, azimuthal mapping measurements on clean W(110) with the improved instrumentation is needed to support this identification. On this basis, information obtained to date supports the hypothesis that scattering by plasmon excitation occurs predominantly before the electron enters the crystal. The investigation of other principal azimuths of W(110) - 0[1/2] is in progress.

III. Determination of nature and structure of surface layers with low energy electron diffraction (E. Bauer)

It is well known now that the electron diffraction patterns of "clean" surfaces of many crystals show a lateral periodicity different from that of the bulk of the crystal. For the interpretation of such patterns it is essential to understand their formation mechanism and to have an understanding of the interaction mechanism of the electron beam with the crystal. Of particular importance is the understanding of the influence of inelastic scattering on the penetration depth of the electron beam, because inelastic scattering determines ultimately the thickness of the surface layer which contributes to the (elastic) diffraction pattern. With these objectives in mind the Si(111) surface was chosen for the following reasons: (1) The "clean" Si(111) surface produces several different diffraction patterns depending upon pretreatment; (2) The electronic energy band structure of silicon is well known. Therefore, it can be expected that the inelastic scattering due to single electron interband transitions can be explained in terms of the electronic energy band structure of the crystal; (3) The collective electron excitations (plasmons) in silicon are known to be free-electron gas-like. This is a consequence of the large energy separation of the valence band which contains the four "free" electrons from the next lower energy level (L level); and, (4) Silicon does not alloy with many metals and provides, therefore, an ideal substrate for metal films for the study of the inelastic scattering of slow electrons by metals.

The problems studied and the results obtained during this report period are as follows:

(1) The kinetics of formation of the Si(111) - 7x7 and Si(111) - $\sqrt{19} \times \sqrt{19}$ R(23.5°) LEED patterns, previously ascribed to the clean surface. The problem was studied by measuring the intensities, I, of characteristic spots in the LEED pattern as function of distance, x, from the crystal supports after various heating times, t, and temperatures, T. The results show clearly that in the case of the Si(111) - 7x7 pattern I(x,t,T) can be described by a one-dimensional diffusion equation with the crystal mount as source. The measurements were performed in the temperature range from about 700° to 800°C, in which the diffusion coefficient D_s varies from .5 to $4 \cdot 10^{-4}$ cm^{2}sec^{-1}. From the temperature dependence of D_s an activation energy of 50 kcal/mole follows. The large value of D_s excludes volume diffusion but is compatible with a surface diffusion mechanism. The $\sqrt{19} \times \sqrt{19}$ R(23.5°) pattern, however, is formed both by surface and volume diffusion, at least in the crystal investigated which previously had been doped with Ni. Due to the mixed diffusion and the unfavorable geometry of the crystal no diffusion parameters could be determined in this case.

Nevertheless, the experiments clearly indicate that both the $\sqrt{19} \times \sqrt{19}$ R(23.5°) and 7x7 LEED patterns are formed by diffusion processes of impurities (Ni and very likely Fe, respectively, according to Auger electron spectroscopy) from the bulk and/or from the crystal mount to the crystal surface. This strongly supports the previously proposed surface impurity layer interpretation of the LEED patterns (see Encl. 2 of 2nd Quarterly Status Report).

(2) The energy loss spectrum of slow electrons (30-150 eV energy) scattered from Si(111) surfaces. The purpose of these measurements was 1) to obtain an understanding of the energy loss mechanisms of slow electrons in crystals in terms of single electron transitions and plasmon excitations, and 2) to determine the influence of the surface structure on the energy loss spectrum. The experiments were performed for various angles of incidence (θ,ϕ) onto the crystal; the electron current scattered backward into a cone of 90° was energy-analyzed with an energy resolution of .8 eV. The measurements were hampered by some artifacts, such as charging of insulators in the energy analyzer, so that only preliminary data can be reported. The sources of the artifacts are being eliminated at present by proper shielding. The more significant results are as follows: a) the energy distribution from below 0 to about 10 eV energy loss shows considerable structure which changes with θ and ϕ and to a lesser degree with the surface structure. It can be explained in terms of nondirect transitions between the valence and conduction bands of bulk Si; b) the surface plasmon excitation in Si at about 10.5 eV is abnormally low irrespectively of the surface structure; it increases only slightly with the polar angle of incidence θ; c) the threshold for volume plasmon excitation in Si is considerably higher than predicted by theory assuming that the four valence electrons per atom contribute to the "free electron gas". These preliminary results clearly indicate the need for a more sophisticated theory and more detailed measurements which are planned for the next report period.

(3) The energy loss spectrum of slow electrons (30-50 eV) energy scattered in epitaxial Al films on Si(111) surfaces. The purpose of these measurements was to determine whether the abnormalities in the plasmon excitation in Si by slow electrons were typical for Si or a general aspect of plasmon excitation by slow electrons. The Al films were deposited in situ and grew parallel to the substrate, i.e., with a (111) orientation. The measurements were performed as in Problem (2). The most important results are: a) surface plasmon excitation in Al is much stronger than the volume plasmon excitation as expected from theory; this is in strong contrast to Si where the reverse is true; b) the threshold for volume plasmon excitation is much larger than predicted by theory assuming that each atom contributes three electrons to the "free electron gas"; this is in agreement with Si; c) the energy dependence of the probability for surface plasmon excitation shows an abnormality near the threshold for volume plasmon excitation. The comparison of these results with those listed under (2) clearly demonstrates the poor theoretical understanding of the inelastic scattering of slow electrons at present, even for surfaces which are "simple" from the point of view of collective electron behavior and points out the need for detailed experimental work to help obtain a better understanding.

IV. Relation between structure and electron emission properties of work function reducing layers on W{110} surface (G. Turner and E. Bauer)

The ultrahigh vacuum electron microscope (UHVEM) and the many problems associated with its conversion to a bent beam system have been the object of continued effort during this report period. In order to draw quantitative conclusions concerning adsorbate influence upon surface structure and work function changes, it would be most convenient to combine low energy electron diffraction (LEED) and low energy electron diffraction microscopy (LEEM) with emission microscopy. This can be done in the UHVEM bent beam system where the illuminating beam is separated from the imaging beam by a magnetic deflection field. The separation is necessary to allow filtering of the inelastically scattered electrons in the image while at the same time not reducing the intensity of the illuminating beam.

In changing over to a bent beam system, many problems have arisen, most of which can be separated into three main areas: (1) system alignment, (2) image distortion, resulting from deflection field, and (3) image intensity.

The problems of system alignment are compounded by the presence of extraneous magnetic fields. This is especially true in the region of the objective lens and the filter lens where the electron energies are very low (i.e., a few electron volts). One of these extraneous magnetic fields has been reduced by the incorporation of redesigned deflection pole pieces and yoke to minimize stray fields. Another system alignment problem is in the positioning of the center electrode of the filter lens. This lens operates at the second magnification maximum in order to separate the inelastic from the elastically reflected electrons. This operating point places some very strict requirements, not only on the maximum stray magnetic fields which can be tolerated in the region of the lens, but also on the mechanical positioning of the center electrode with respect to the optical axis. As a consequence, the filter lens-center electrode motion device has been modified to produce a more sensitive and reproducible control. Both of these improvements, the new deflection yoke and the modified position control on the filter lens, will allow easier and better alignment of the system.

The image distortion resulting from the 60° deflection of the imaging beam in the bent beam setup has been compensated for (at low magnifications) by use of the magnetic quadrupole lens. It appears also that proper excitation of a single quadrupole lens, positioned immediately after the deflection field, should properly compensate image distortion at all magnifications. However, the quadrupole lens has a large residual magnetic field and a large stray magnetic field when excited which further complicates alignment. This problem is being investigated.

At higher magnifications, and with proper filtering of the inelastically scattered electrons, the reduced image intensity at the fluorescent screen becomes a problem. To help alleviate this, an external 3-stage image intensifier has been mounted and checked out. Although a large luminous gain is inherent in the image intensifier, transfer lenses and vacuum windows reduce the overall gain to some extent. An electron channel multiplier is also being incorporated into the system for study. This will be mounted inside the imaging column adjacent to the fluorescent screen and will also give a large gain in electron intensity. The mounting hardware has been designed and is being built. Either or both of these image intensifying devices will permit the UHVEM to work in the LEED and LEEM modes of operation where normal image intensity is extremely low.