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LASER SURFACE INTERACTIONS: CREATION AND DETECTION OF ATOMICALLY CLEAN SURFACES

Principal Investigator:
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Abstract

It is shown that high power Q-spoiled LASERs offer an interesting method for obtaining clear surfaces in vacuum. However, complete removal of oxygen and carbon contamination from nickle surfaces by LASER bombardment at 100 MW/cm^2 produced irreparable surface damage that is attributed to filamentizing of the LASER beam and/or to non-uniform surface reflectivity. On the other hand, application of the technique at 30 MW/cm^2 successfully removed the (7 × 7) satellite structure from (111) silicon surfaces.

I. INTRODUCTION

One of the obvious, but difficult, tasks that must be performed prior to experiments in surface physics is the creation of atomically clean surfaces. Presently available methods, such as bulk heating, chemical etching, sputtering, electron scrubbing, and vacuum cleavage, have either limited application or other disadvantages.[1] These are summarized below.

Heating to high temperature is restricted to targets whose surface impurities have a higher vapor pressure than the pure material. At high temperature, impurities such as carbon diffuse from the bulk to the surface. In addition to thermal etching, which has been observed,[1] cooling to a desired experimental temperature may require more time than the flux of residual constituents of the vacuum system allows.

Though more versatile, low energy sputter ion cleaning may result in permanent entrapment of noble gas atoms,[2] in preferential etching,[1] in facets,[3] and in increased sticking probability for reactive gaseous impurities.[4] Futhermore, introduction of an ion gun into the vacuum is not always convenient.

Low energy electron scrubbing is limited to those contaminating absorbate-substrate systems with a high cross section for desorption. For example, the maximum efficiency of desorption for a favorable system, such as oxygen on molybdenum, is 10^{-4} atoms/electron.[5] In this case, 10 ma/cm^2 electron current density at approximately 100 eV for 10 seconds is required to remove one monolayer. On the other hand, intense low energy electron beams can heat surfaces to temperatures high enough for surface (and surface impurity) vaporization. As shown in the following section, the usual high temperature problems associated with bulk heating can be alleviated by pulsed surface heating if certain conditions are met with regard to power, maximum surface temperature, and thermal properties of the substrate. Unfortunately, it appears that these conditions cannot be met by low energy pulsed electron heating. In either scrubbing or surface heating, the necessary low energy high electron current may be inconvenient and may be accompanied by unacceptably large amounts of contaminates.

A new method for cleaning solid surfaces in vacuo has become feasible through the advent of high power pulsed LASERs. It is well known that the electromagnetic energy flux contained in a focused LASER beam is sufficient to remove macroscopic quantities from the surface by vaporization.[6] If feasible, the advantages of LASER cleaning would be:

(a) No foreign atoms are introduced into the surface.

(b) The cleaning tool does not spoil the vacuum conditions, since the LASER is located outside the system, and the beam is introduced through an optically transparent port.

(c) If the duration of the LASER pulse is short, only the surface is heated to high temperatures. Heating of the bulk of the specimen by thermal conduction from the surface is negligible. Hence, bulk impurities cannot migrate to the surface.

(d) Following a pulse, the heated surface layer will cool to ambient in less than a millisecond. Therefore, investigation can begin immediately after cleaning, thereby avoiding the possibility of recontamination by background gases during the cooling phase.

(e) The amount of material removed per unit surface area can be controlled by changing the intensity and/or the duration of the LASER pulse.

Disadvantages of LASER cleaning might be:

(a) The LASER light may affect the surface unevenly; it may produce microscopic craters[7] and local melting.

(b) Unacceptable surface disorder may result from the rapid quenching noted under (d) above. This difficulty may be alleviated by subsequent annealing at a temperature considerably less than that required for impurity vaporization.

(c) Many of the above advantages will not apply to optically transparent media. However, high energy flux phenomena may discount this limitation.

Our experimental program to investigate these advantages and disadvantages is given below.

II. THEORETICAL MODEL OF SURFACE TEMPERATURE VERSUS TIME

During LASER bombardment, the layer of the surface within the electromagnetic skin depth becomes a volumetric heat source. Since the skin depth for good electrical conductors — such as copper — is small compared to the characteristic length for thermal diffusion during the LASER pulse, the volumetric source can be replaced by an energy flux at the surface. This approximation obviously does not apply to optically transparent media.

Linear geometry is assumed in which heat is removed from the surface by conduction in the direction opposite to the influx of energy, and the dimension of the specimen in this direction is taken as infinite. Radiant heat transfer from the surface is neglected, but *a postiori* calculation shows this to be a secondary consideration.

Solution of the heat conduction equation for constant flux yields the following expression for the surface temperature during the bombardment phase.[8]

$$\theta\ (0 < t < T) = \frac{2F_0}{K}\left(\frac{kt}{\pi}\right)^{1/2} \qquad (1)$$

where

θ = temperature measured from ambient; $\theta\ (0) = 0$

F_0 = unreflected energy flux

K = thermal conductivity = 0.93 cal $\mathrm{cm}^{-1}\,{}^\circ\mathrm{C}^{-1}\,\mathrm{sec}^{-1}$ for Cu

k = thermal diffusivity = 1.14 $\mathrm{cm}^2/\mathrm{sec}$ for Cu

t = time

T = period of bombardment

Following bombardment, the surface temperature as a function of time is

$$\theta\ (t > T) = \frac{2F_0}{K} \left(\frac{kt}{\pi}\right)^{1/2} \left[1 - \left(1 - \frac{T}{t}\right)^{1/2}\right] \tag{2}$$

Since T is small in comparison to a convenient cooling time, the right hand side of (2) can be expanded as a function of T/t. Only the first term in the expansion is retained.

$$\theta(t >> T) = \frac{F_0 T}{K} \left(\frac{k}{\pi t}\right)^{1/2} \tag{3}$$

Equation (3) can be conveniently expressed in terms of the surface temperature at the end of the bombardment period, $\theta(T)$.

$$\frac{\theta(t >> T)}{\theta\ (T)} = \frac{1}{2} \left(\frac{T}{t}\right)^{1/2} \tag{4}$$

These results are applied to the case of LASER cleaning of copper, whose most tenacious and stable oxide, Cu_2O, decomposes at approximately 1800°C. According to Equation (1), 6×10^7 watts/cm^2 must be coupled to the copper surface in order to raise the temperature to 1800°C in 10^{-8} seconds. Since one-Joule Q-spoiled LASERs are commercially available, the flux requirements given above can be delivered to a target area of 0.1 cm^2

even in the presence of significant reflection. Investigation of Equation (4) shows that the surface will cool (by conduction only) to ambient in less than a millisecond following the pulse. Hence, investigation of the clean surface can begin immediately following pulsed LASER cleaning with no danger of surface temperature variation during the measurements. It should be noted that thermal radiation at the maximum temperature, assuming an environment at 0°K and an emissivity of unity, is insignificant compared to the incident energy flux (59 w/cm^2 radiated compared to 10^7 w/cm^2 incident). Similarly, removal of the incident energy by thermal radiation at the maximum temperature would require 170 seconds following bombardment. Thus, radiant transfer can be neglected during both heating and cooling phases.

III. APPARATUS

A schematic diagram of the experimental apparatus is shown in Figure 1. The primary components are a low energy electron diffraction (LEED) device* and a Korad Q-switched water-cooled ruby LASER. The photon pulse was 20 nsec FWHM (full width at half maximum). The energy delivered to the target was measured by a beam-splitter-diffuse scatterer-photodetector method.[9] The system was calibrated by calorimetric measurement, and energy output was varied between 0.1 and 1.0 J by adjusting the concentration of copper sulfate in distilled water, which served as the beam attenuator. A 30-cm focal length lens, mounted outside of the vacuum system, focused the beam in front of the target surface, yielding a spot diameter at the surface of approximately 0.2 cm^2. Care was taken to insure that the above apparatus did not contribute to the resonant LASER cavity.

Observation of purposely contaminated surfaces and supposedly clean surfaces was accomplished by LEED measurement. The principal observable was the fluorescent intensity, measured by a telephotometer of a diffracted beam from a clean or partially contaminated surface. Sequential treatment, by the LASER and LEED beams, required rotation of the target between the glass (LASER) port and the flang-mounted (LEED) electron gun. Hence, a pressure of 2×10^{-10} Torr was maintained throughout any particular investigation except when a contaminating gas was purposely bled into the system through a controlled leak valve. Constituent and contaminating gases were monitored by a residual gas analyzer.

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*The LEED apparatus was manufactured by Varian Associates, Inc., and was augmented by a small quartz window for introduction of the photon beam and by a shield to insure that material removed from the target did not contaminate the fluorescent screen.

IV. EXPERIMENTAL TECHNIQUE AND RESULTS

A. Removal of Oxygen from a Nickel Surface

The (100) face of a nickel crystal was mechanically and electrolytically polished, and a thermocouple was spot-welded to the edge of the crystal for temperature monitoring. The crystal was then subjected to prolonged heating at 700°C at 10^{-10} Torr pressure. After this procedure, the C(2 × 2) diffraction pattern, which is believed to be a result of sulphur contamination,[10] was observed. A clean nickel surface (Figure 2) was then obtained by argon ion bombardment followed by annealing.[11] With the target at room temperature, oxygen was admitted into the vacuum system until a half monolayer of oxygen had formed on the clean Ni (100) face, which resulted in the well-known C(2 × 2) diffraction pattern[12] shown in Figure 3.

LASER pulses at 10 to 30 MW/cm^2 produced pressure surges to 10^{-9} Torr, and the intensity of the diffracted beams increased at the expense of background. The partial pressure gauge indicated that the surges consisted of N_2, CO, H_2, CO_2, H_2O, and hydrocarbons, which are the main background gases in the system. We conclude that these gases were weakly bonded to crystal and interior chamber surfaces and were desorbed by the LASER light. The presence of such gases has been detected before through bulk heating desorption experiments.[13] After ten pulses the pressure surges were reduced, indicating the near absence of the weakly adsorbed gases on the surface.[9]

Exposure of the crystal to ten pulses at 40 MW/cm^2 decreased the intensity of those diffraction beams attributed to the oxygen C(2 × 2) structure. There was no appreciable change in the beams associated with a clean Ni surface, and no surface damage was apparent. After annealing for 5 minutes at 200°C, the intensity of the C(2 × 2) beam increased to its original value. Since it has been shown experimentally that oxygen does not diffuse into the bulk at these temperatures,[12] we attribute the temporary decrease in intensity to local surface melting, followed by rapid quenching, with no loss of oxygen from the surface. Reordering of the oxygen surface structure occurred during the annealing phase.

The intensity of the C(2 × 2) beams was permanently reduced after ten pulses at 60 MW/cm^2. We attribute this to the desorption of oxygen or of NiO, as was reported for tungsten.[14] Although surface damage could not be detected in situ, ejection craters could be observed by optical microscopy after removal from the vacuum chamber (Figure 4).

A single pulse of 80 MW/cm^2 power density, focused onto an undamaged area of the crystal surface, produced a reduction in beam intensity and visible damage. Repeated shooting produced additional oxygen desorption as indicated by the decrease in the intensity of the oxygen C(2 × 2) spots (Figure 5). At this stage, surface damage was quite severe (Figure 6).

The pulses of 120 MW/cm^2 power density caused complete desorption of oxygen. After annealing the "clean nickel" diffraction pattern was obtained (Figure 7). However, the spots were diffuse. Annealing for several hours at 600°C made the spots less diffuse, but the original sharpness and intensity was not regained. The surface was atomically clean but heavily damaged.

B. Sulphur on Nickel

Sulphur contamination[10] appears on nickel surfaces after the high temperature annealing phase of the cleaning operation. It is identified by the C(2 × 2) diffraction pattern (see above). Cyclic exposure of this structure to 20 LASER pulses in the 120 MW/cm^2 power density range and annealing for several hours produced an atomically clean surface, as indicated by the diffraction pattern. However, observation under the microscope revealed considerable surface damage. Firing the LASER with the crystal at 800°C, or using multiple spike (conventional mode) instead of Q-spoiled LASER pulses, did not reduce surface damage.

C. Silicon

The (111) face of a silicon crystal was mechanically and chemically polished and, after annealing under vacuum at 1000°C for 6 hours, the (7 × 7) diffraction pattern[15] was observed (Figure 8). The surface was then exposed to a succession of LASER pulses. As the power density was increased from 10 to 40 MW/cm^2, the intensity of the satellite spots decreased, as illustrated in Figures 9a, 9b, and 9c. There was no visible surface damage. Annealing at 1000°C for 5 minutes restored the ordered structure to that of Figure 8.

A single LASER pulse at 60 MW/cm^2 produced the diffraction pattern shown in Figure 10. Annealing again gave the ordered (7 × 7) structure. No surface damage could be observed under the microscope. However, repeated firing in this power density range produced visible damage, as shown in Figure 11.

V. CONCLUSIONS

A. We have demonstrated that oxygen or sulphur contamination can be removed successfully from the (100) face of nickel by exposing it to high power LASER pulses (120 MW/cm^2). However, the cleaning operation is accompanied by irreparable surface damage, as observed under the optical microscope and identified by the deterioration of the low energy electron diffraction pattern.

B. Surface damage, which consisted of craters and pits caused by local melting and possibly ejection, could not be removed by annealing. It is assumed that surface defects (i.e. areas of low reflectivity) and/or high power density filaments[16] in the LASER beam are the primary sources of damage. Since the latter are attributed to non-uniformity in the ruby rod, there is a possibility that newly developed or improved LASERs may eliminate the problem. Since reflectivity usually decreases with temperature, lack of sufficient surface uniformity could continue to pose a problem even if uniform LASER beams can be developed.

C. It has been shown that relatively low power density LASER pulses (approximately 30 MW/cm^2) can remove the (7 × 7) satellite structure from the (111) surface of silicon without damaging the surface. The disappearance of this structure after quenching may be attributed to the loss of long-range order in the surface structure due to the formation of out-of-phase patches with dimensions smaller than the coherent length of the electron.[17] This change in the surface structure is more analogous to melting than to evaporation, since repeated bombardment at this LASER power density does not result in any visible pits on the surface.

D. Contamination of solid surface by background gases, mainly CO, H, H_2O, and hydrocarbons, is inevitable within hours even with a 10^{-10} Torr vacuum. These gases can be desorbed by a relatively low power density LASER pulse (30 MW/cm^2).

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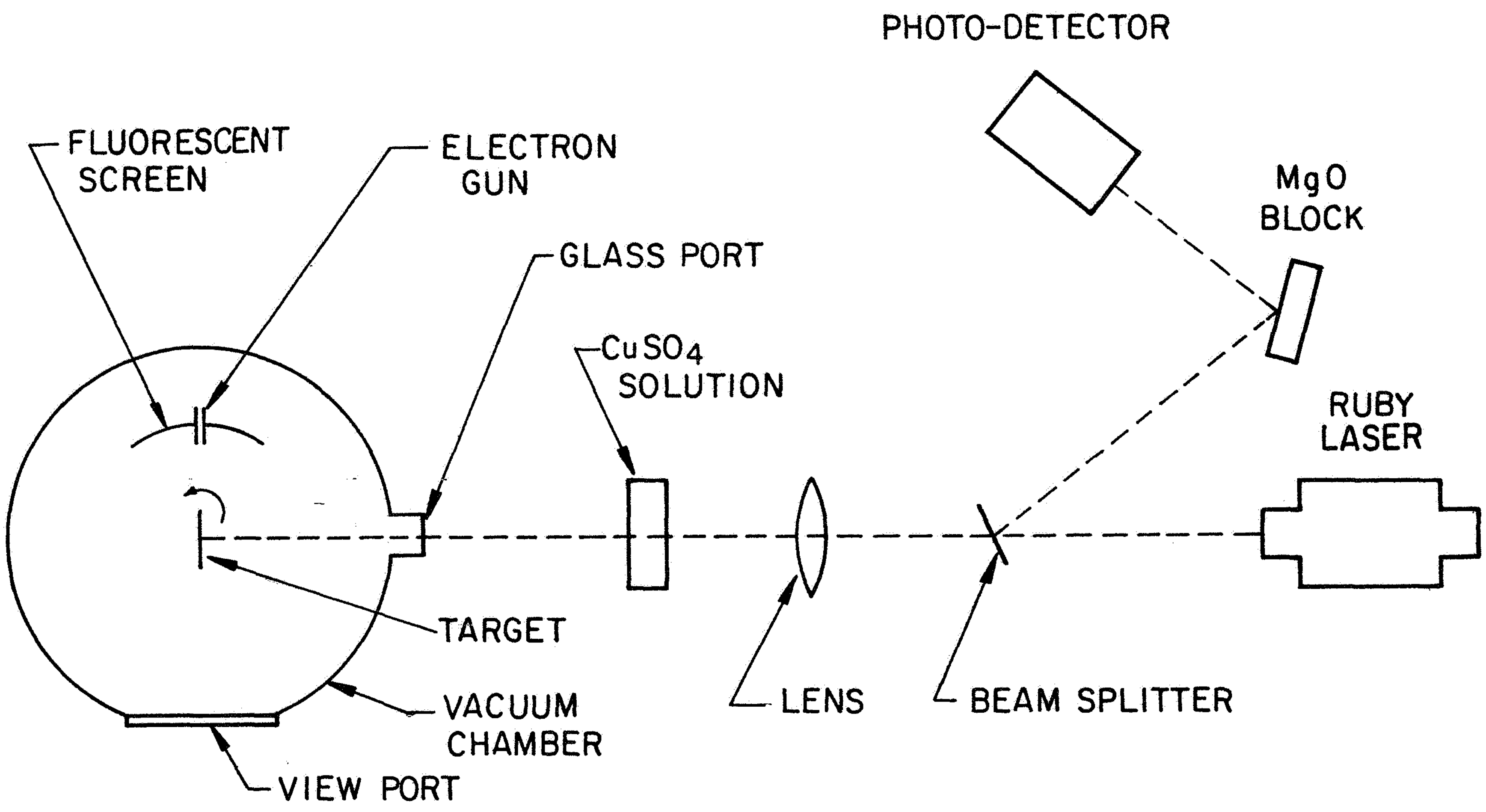


Figure 1: Schematic diagram of the experimental setting. The calibration constant for the photodetector is 2.8 Joules/volt.

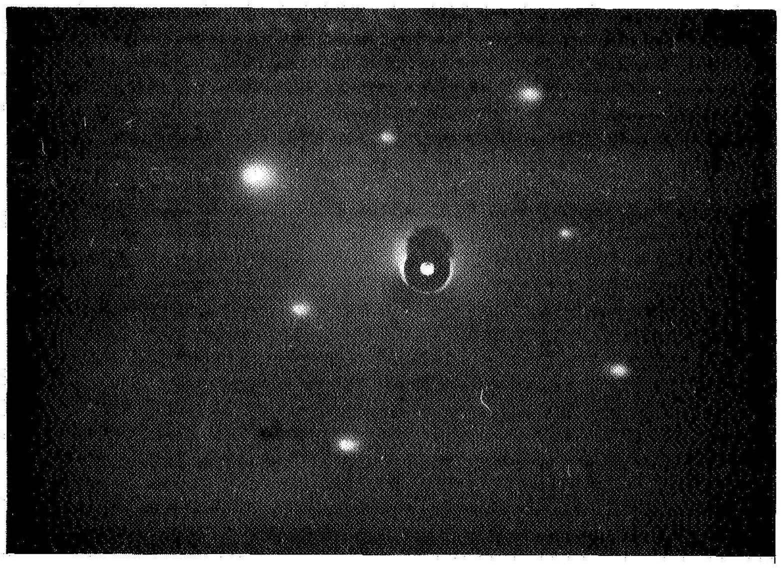


Figure 2: Diffraction pattern of a clean Ni[100] face. Electron energy is 150 eV.

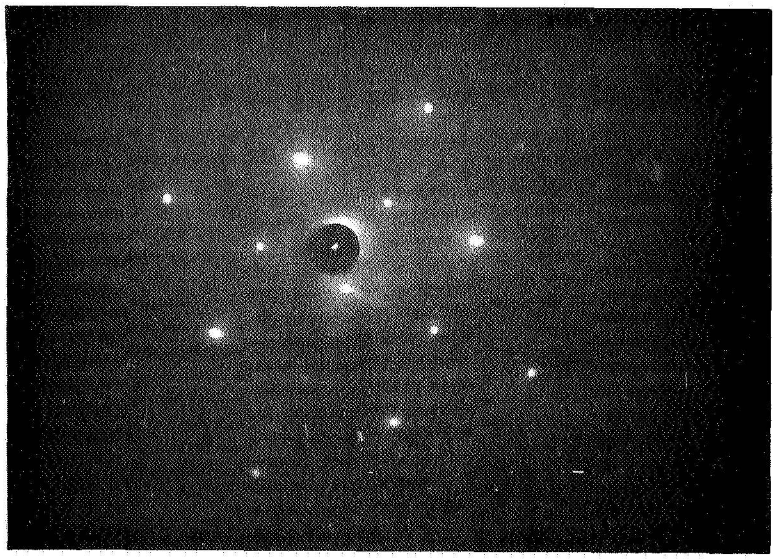


Figure 3: C(2 × 2) diffraction pattern after oxygen exposure. Electron energy is 133 eV.

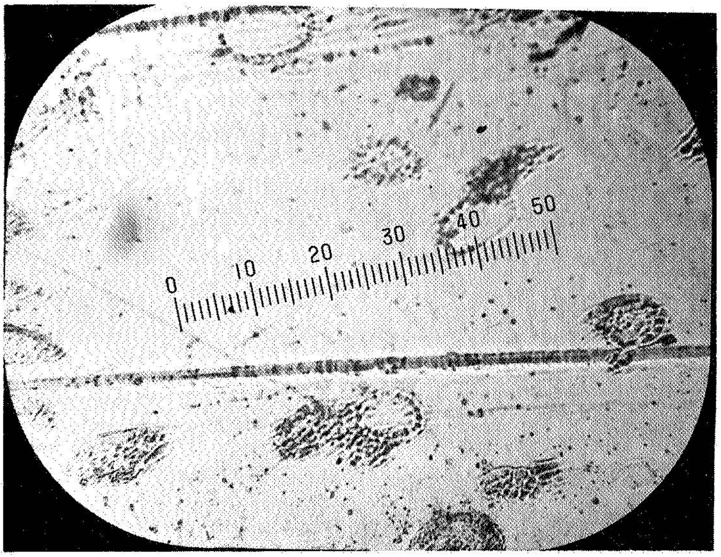


Figure 4: Microtopography of the initial damage stage. Magnification is × 200. This area was fired with a power density of approximately 60 MW/cm^2.

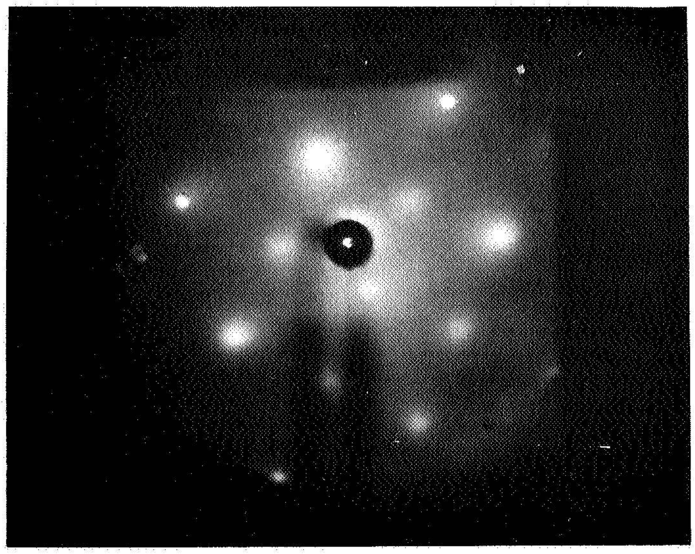


Figure 5: C(2 × 2) diffraction pattern at an intermediate stage of oxygen desorption. The intensity of all the diffraction spots decrease and become more diffuse. Electron energy is 133 eV.

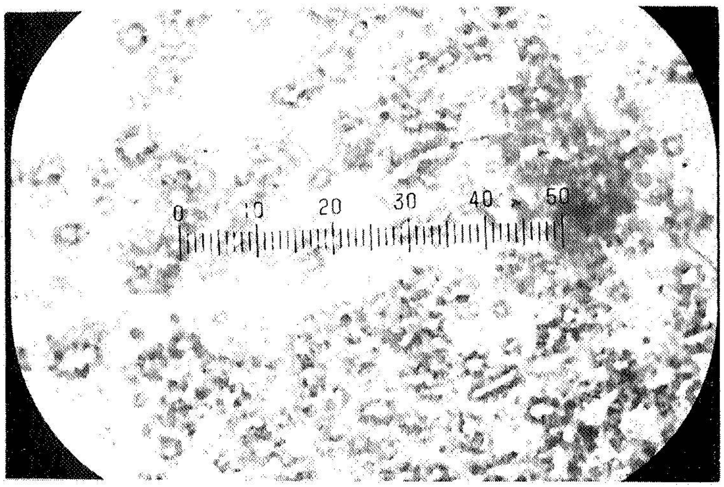


Figure 6: Microtopography of the surface conditions that gives the diffraction pattern in Figure 5. Magnification is × 100.

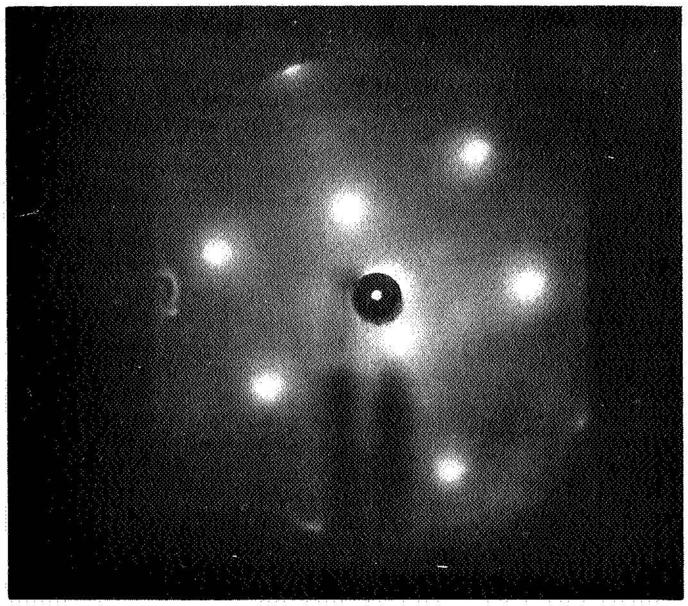


Figure 7: The diffraction pattern of a clean (100) Ni face after ten shots at a power density of 120 MW/cm^2, followed by annealing at 200°C for 5 minutes. Electron energy is 133 eV.

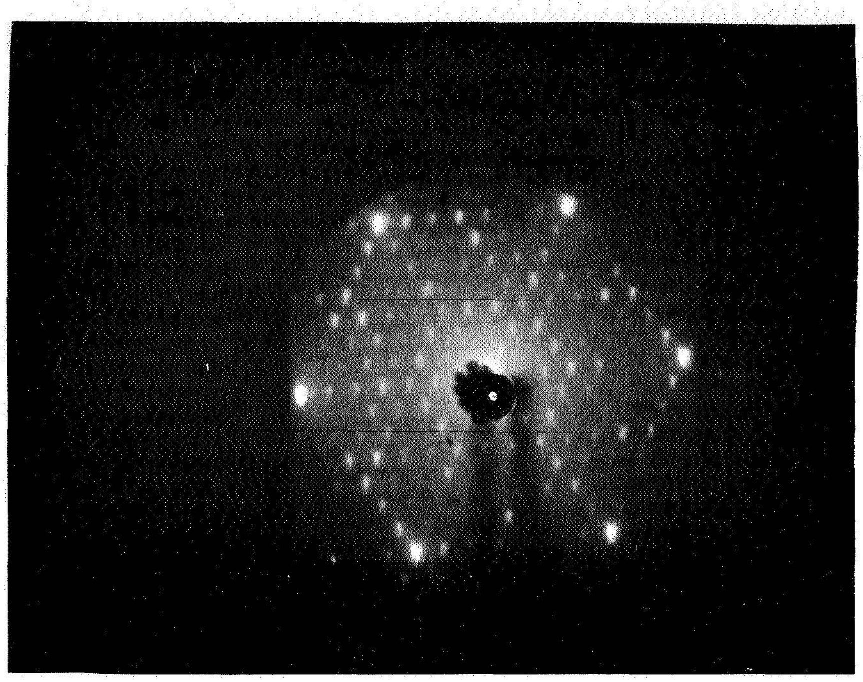
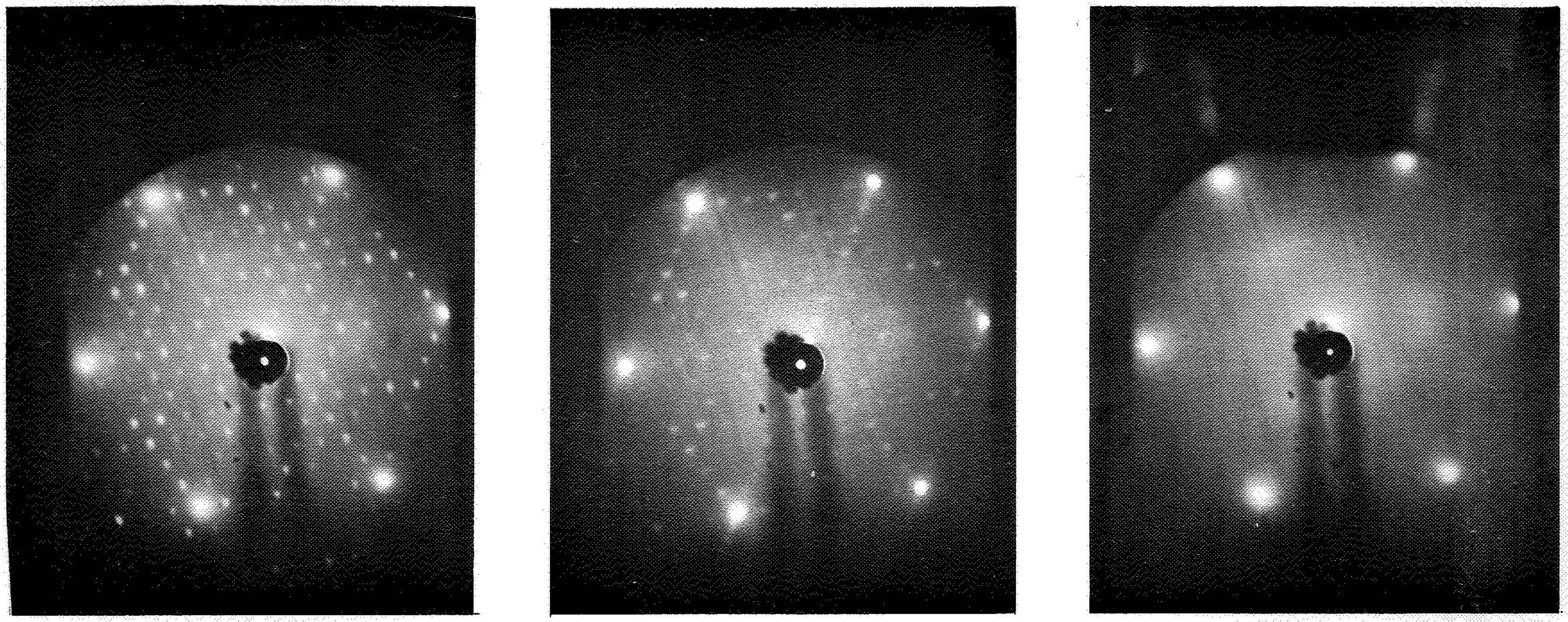


Figure 8: Diffraction pattern from a clean Si(111)-7 surface structure. Electron energy is 50 eV.



(a) (b) (c)

Figure 9: The effect of a succession of laser pulses on a well annealed Si(111)-7 structure. Diffraction patterns in a, b and c correspond to power densities of 10, 20, and 40 MW/cm^2, rsspectively.

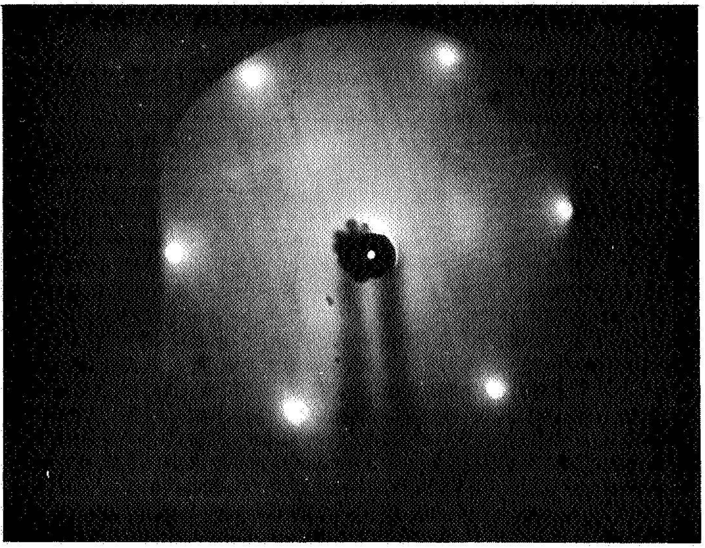


Figure 10: Diffraction pattern of Si(111)-7 structure after a single pulse at 60 MW/cm^2 power density.

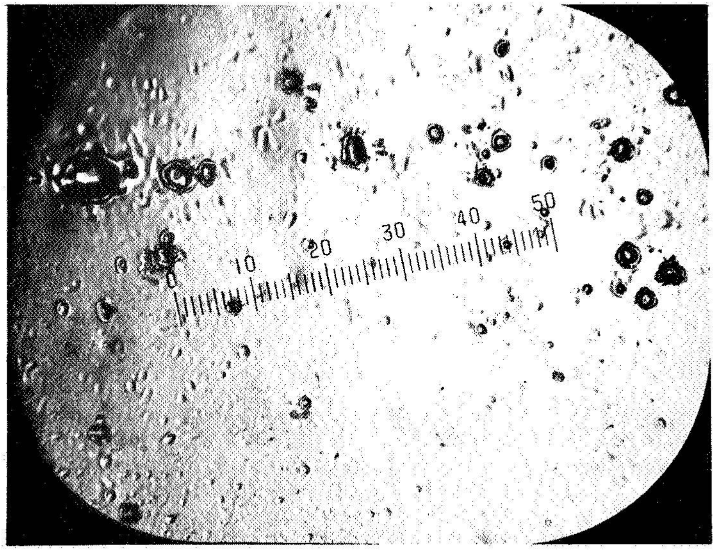


Figure 11: Microtopography of the silicon surface after repeated firing with power density of 60 MW/cm^2. Magnification is × 50.