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IN NON-AQUEOUS SOLVENTS: A SURFACE SCIENCE APPROACH

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Scherson, D.A.

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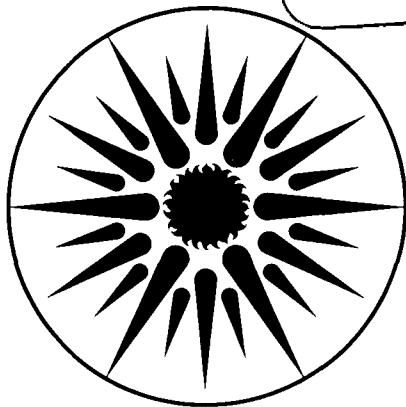
Spectroscopic Studies of the Passive Film on Alkali and Alkaline Earth Metals in Non-Aqueous Solvents: A Surface Science Approach

D.A. Scherson, G. Chottiner, P. Herrera-Fierro
and X. Xing

October 1987

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**SPECTROSCOPIC STUDIES OF THE PASSIVE FILM
ON ALKALI AND ALKALINE EARTH METALS
IN NON-AQUEOUS SOLVENTS:
A SURFACE SCIENCE APPROACH**

Final Report

October 1987

by

**Daniel A. Scherson
Gary Chottiner
Pilar Herrera-Fierro
Xuekun Xing**

Case Center for Electrochemical Sciences and
The Departments of Chemistry and Physics
Case Western Reserve University
Cleveland, OH 44106

for

Technology Base Research Project
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4528410 with the Lawrence Berkeley Laboratory.

ABSTRACT

The feasibility of experiments in which, sub-, mono- and multilayer coverages of alkali metal are first vapor deposited on a well characterized single crystal specimen and then exposed to a non-aqueous solvent in ultra high vacuum has been demonstrated using K/Ag(111)-propylene carbonate PC, as a model system. The results obtained have indicated that Ag(111) exhibits no affinity for propylene carbonate at room temperature as monitored by work function $\Delta\phi$, measurements and Auger electron spectroscopy, AES. In contrast, sizable changes in $\Delta\phi$ were observed for similar experiments involving Ag(111) covered by K even when the latter was present at coverages well below a monolayer. The AES spectra of the K/Ag(111)-PC surfaces layer showed C, and O peaks indicating that the presence of K on the surface leads to an increase in the sticking coefficient of PC on Ag(111). A series of AES spectra recorded after such reacted layers were heated at different temperatures provided evidence that all the reaction products including K can be desorbed from the surface at about 600° rendering a clean, highly ordered Ag(111) surface.

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The research conducted during the second year of this project has been focussed mainly on the implementation and further refinement of the techniques associated with each of the steps involved in the preparation and characterization of synthetic alkali metal passive films. The progress made in each of these areas may be summarized as follows:

I. Ultra high vacuum-Electrochemical cell transfer system

The design and construction of the instrumental array involved in the synthesis of alkali metal passive films and their further evaluation in actual electrochemical environments has essentially been completed. A schematic diagram of the ultra high vacuum system in its present form is shown in Fig. 1. It consists of two independently pumped stainless steel UHV chambers connected by means of a straight-through all-metal valve. Chamber A, referred to hereafter as main, houses a VSW hemispherical electron energy analyzer, a Perkin Elmer low energy electron diffraction LEED unit, an electron gun for Auger measurements, an Ar-ion sputtering gun, a Dycor M200M mass spectrometer for the analysis of residual gases and thermal desorption spectroscopy measurements, and a precision XYZ, Huntington manipulator coupled to a differentially pumped rotary feedthrough with a simple cryostat for the cooling of specimens down to liquid nitrogen temperature (see Inset Fig. 1). Chamber B or auxiliary, is a multiport unit supported on a custom designed aluminum superstructure which houses three independent manipulators involved in the transfer of specimens between the main and auxiliary chambers and in the electrochemical experiments.

The single crystals are mounted on a holder that can be attached to or detached from either one of the two vertical bellows-type manipulators. These operations are performed by means of a special tool installed at the tip of the horizontal magnetically coupled manipulator rod that makes it

possible to tighten and loosen the screws which affix the sample holder to either one of the manipulators.¹ This tool also serves as an anchor to secure the holder during the transfer (see Fig. 2). In an actual experiment, the specimen holder is brought into the auxiliary chamber by means of the horizontal magnetically coupled manipulator, M1 (see Fig. 1), and attached to M2 which is equipped with a tilting mechanism. This enables the front surface of the specimen to be placed facing downwards and thus parallel to the counter electrode prior to the formation of the thin layer cell. At the time of submission of this report, a number of sample transfers between the main and auxiliary chambers had been successfully completed.

II. Synthesis of alkali metal passive films

The cleaning and characterization of single crystal surfaces is effected by conventional Ar⁺-sputtering thermal annealing cycles and Auger electron spectroscopy, AES, and low energy electron diffraction, LEED.

Alkali metal layers are vapor deposited onto well-characterized single crystal substrates by resistive heating of commercially available sources (SAES Getters). The system in its current configuration can accept two complete evaporator assemblies.

The dosing of the samples with gaseous compounds including non-aqueous solvents is performed via an independently pumped stainless steel manifold with a capacitance manometer. The gases are introduced into the main chamber through a multicapillary array mounted at the end of a tube. In the present geometry, the single crystal surfaces can be placed very close to the capillary array making it possible to expose the specimens to the gas of interest without a large pressure increase in the main chamber. A shield with a tube of about the same length has been installed around the

quadrupole mass spectrometer so as to reduce contributions due to thermal desorption from areas other than the single crystal surface.

A Kelvin probe is used for work function measurements both in the static and dynamic modes. The latter has been found to afford a rather convenient way of determining end-points for surface reactions.

III. Thermal Desorption Spectroscopy

An IBM-XT computer has been interfaced with the DYCOR M200M mass spectrometer and a Keithley 570 data acquisition system and software developed so as to make efficient utilization of the four data collection modes of the mass spectrometer. This routine is capable of collecting pressure vs. time in an optimized sampling rate-mass resolution mode as well as of monitoring the voltage from the thermocouple connected to the sample. Control of the sample heating is currently conducted manually. Work is now in progress, however, to control the heating automatically with an Omega temperature programmer coupled to a voltage controlled phase controller. The complete TDS system is shown schematically in Fig. 3.

IV. Standardization of the System

As a means of assessing the overall performance of the components involved in the proposed experiments, a number of measurements were performed using Ni(111) as the substrate. This surface appears particularly suited for this purpose as some aspects of its behavior have been thoroughly characterized. In particular, the AES spectra obtained after introduction of the sample into the main chamber exhibited, as expected, carbon and sulfur impurities (see Fig. 4). These were removed by well developed procedures involving high temperature treatment in the presence of oxygen and Ar⁺-sputtering. The atomically smooth character of the surface after the ion bombardment was restored by thermal annealing and monitored by LEED. This treatment was found to induce segregation of

impurities from the bulk to the surface of the specimen, making it necessary to perform several sputtering-annealing cycles until an AES spectrum characteristic of clean nickel exhibiting sharp LEED patterns was obtained. It is interesting to note, that the series of spectral features in the range between 100 and 400 eV which could be clearly seen only in very clean and highly ordered Ni(111) specimens, (see Fig. 4) are not associated with Auger transitions but rather with diffraction from the substrate as reported originally by Becker and Hagstrum.²

Exposure of clean and well-ordered Ni(111) surfaces to 4 L of O₂ were found to yield LEED patterns (see Fig. 5) consistent with the presence of an ordered overlayer of dissociatively chemisorbed oxygen on the surface as proposed by other workers.³

The work function, $\Delta\phi$ of a well characterized Ni(111) surface was monitored as a function of exposure of the crystal to CO and the results obtained are shown in Fig. 6. The difference in $\Delta\phi$ between the clean and CO saturated Ni(111) surface was found to be about 1.2 eV which corresponds almost exactly to that reported by Ertl and coworkers.⁴ Also in agreement with literature data⁴ was the peak temperature in the thermal desorption spectra of CO on the Ni(111) surface.

In additional measurements, LEED patterns for the less studied K/Ni(111) system given in Fig. 7, have provided evidence for the formation of a superstructure for low coverages of the adsorbate on the surface. The corresponding AES spectra obtained before and after vapor depositing the alkali metal are shown in Fig. 8. The K deposits, at least within the limits of detectability of AES, were found to be free of impurities as no other spectral features besides those associated with K and Ni could be detected in the spectra. It may be noted that preliminary TDS experiments

have indicated that the temperature associated with the thermal desorption of CO is displaced toward higher values when compared with the K free surface.

These data indicate that all the system components as well as the methodologies involved in these experiments appear to yield satisfactory results and therefore may be expected to afford reliable data for the alkali (or alkaline earth) metals/non-aqueous solvent systems to be examined in the proposed research.

V. The Ag(111)/K/Propylene Carbonate Interface: A Model System

The feasibility of experiments in which, sub-, mono- and multilayer coverages of alkali metal are first vapor deposited on a well characterized single crystal specimen and then exposed to a non-aqueous solvent in ultra high vacuum has been demonstrated. The Ag(111)/K/propylene carbonate interface was chosen as a model system based on the following considerations:

- i) The Ag(111) surface has been found to be thermodynamically stable and shown to exhibit essentially no affinity for any of the solvents examined, and a variety of small gaseous molecules that could be formed as degradation products of reactions between the alkali metal and the solvent.
- ii) Propylene carbonate PC, is believed to be stable over a wide temperature range and has emerged as perhaps one of the most important solvents in applications of technological interest. As will be shown below, PC does not undergo adsorption on Ag(111) and therefore all the reactions observed may be attributed to the presence of the alkali metal on the surface, and
- iii) The Ag(111)/PC interface has been thoroughly characterized by electrochemical techniques including cyclic voltammetry, capacitance measurements, and underpotential deposition,⁵ making it possible to compare

the behavior observed in UHV.

The synthesis and characterization of Ag(111)/K/PC passive layers in ultra high vacuum involved: i) cleaning of the Ag(111) by conventional sputtering-annealing cycles; ii) vapor deposition of potassium on the clean metal surface followed by AES and $\delta\phi$ measurements; iii) adsorption of PC while monitoring $\Delta\phi$; iv) thermal desorption, and v) AES analysis of residual surface species.

The procedure involved in the orientation, cutting and polishing of the Ag(111) crystals was described earlier.⁶ The last polishing stages were performed with 0.25 μ diamond paste followed by 0.05 μ alumina. In these specific experiments the crystals were not subjected to chemical polishing. The AES spectrum of a Ag(111) specimen prepared in this fashion immediately after introduction in the UHV system showed as expected carbon and oxygen impurities (Curve A, Fig. 9). Carbon could be easily removed by annealing, a procedure that was found to induce the segregation of chlorine to the surface. A clean and highly ordered surface as judged by the sharp LEED patterns could be obtained, however, by Ar⁺ sputtering (5 min. at 10 μ A)-annealing (600°C for 20 to 30 min.). The spectrum obtained after this treatment is shown in Curve B, Fig. 9.

The exposure of clean Ag(111) to propylene carbonate in UHV was not found to change the work function nor the AES spectrum indicating that PC does not undergo adsorption on this surface at room temperature.

A series of measurements were conducted in which potassium was vapor deposited on the clean Ag(111) surface. A constant current of 11.05 A was applied to the dispenser while the crystal was positioned directly in front of the oven outlet. Special precautions had to be taken in order to place the crystal in exactly the same position during each deposition as slight

variations in this parameter were found to yield very different results. It was also observed that the electron beam during Auger measurements caused a decrease in the relative intensity of the K(252eV) line (see Fig. 11). It is not clear at this point whether the potassium undergoes desorption or otherwise diffuses into the lattice. The results shown in Fig. 10 appear to be in qualitative agreement with the expected behavior of alkali metal deposits reported by other workers.⁷ The estimated uncertainty represented by the bar in this figure amounts to about 0.1 V.

An attempt was made to study the nature of the potassium film growth by examining the K(252eV) and Ag(351eV) Auger line intensities as a function of the deposition time, D_t . Representative Auger spectra obtained for four different values of D_t are shown in Fig. 12. An analysis of the peak heights based on the complete series of spectra yielded for both elements approximately straight lines with opposite although different slopes. The quality of the data, however, was not high enough to elucidate unambiguously the mechanism of film growth. A calculation based on the relative intensities of the two metal Auger lines indicates that Curve C in Fig. 12 has an associated potassium surface concentration of approximately 20-30%. If it is assumed that the mean free path of 250 eV electrons is around 6 to 7 Å this would correspond to approximately one monolayer of K. This conclusion appears to be in excellent agreement with the work function results shown in Fig. 10 for which a monolayer of K is obtained for D_t slightly higher than 1000 s. A composite diagram of the work function (left axis) and relative K surface concentrations as calculated from AES data (right axis) as a function of evaporation time is depicted in Fig. 13. The two curves have been overlapped assuming that the time required for the formation of one monolayer of K on the Ag(111) surface is about 1000 s. The open circles are the results of independent experiments.

In an additional experiment several monolayers of potassium were deposited on the silver crystal. The LEED patterns associated with this surface were found to exhibit a very diffuse six fold symmetry pattern characteristic of a (111) surface with a disordered overlayer. Propylene carbonate was then admitted into the chamber to a pressure of $5 \cdot 10^{-6}$ Torr for approximately 200 s while monitoring the work function. The opening and closing of the leak valve are indicated by the arrows in Fig. 14. As can be clearly seen the work function was first found to decrease slightly, and then to increase almost linearly with exposure time. A constant value approximately 1.9 V higher than that obtained prior to the admission of PC in the chamber was observed ca. 200 s after closing the leak valve. The Auger spectra obtained after the work function stabilized depicted in Fig. 15, shows besides Ag and K quite prominent carbon and oxygen peaks. The same results in a much restricted energy range are given in the Inset. In an effort to obtain information regarding the thermal stability of the reacted layer, several AES spectra were recorded at different heating temperatures. The relative peak intensities for K, O and Ag as a function of substrate temperature shown in Fig. 16 provide evidence that all the products can apparently be desorbed at a temperature of 600°C. It may be noted that K_2CO_3 , a possible reaction product, undergoes thermal decomposition at 900°C at atmospheric pressure to yield presumably potassium oxide, a compound which exhibits a much lower decomposition temperature. The Auger spectrum obtained after the thermal desorption shown in Fig. 17, corresponds to that of clean silver. The arrows indicate the energies at which the peaks associated with K and C would be expected to occur.

VI. Conclusions

The feasibility of experiments in which, sub-, mono- and multilayer coverages of alkali metal are first vapor deposited on a well characterized single crystal specimen and then exposed to a non-aqueous solvent in ultra high vacuum has been demonstrated using K/Ag(111)-propylene carbonate PC, as a model system. The results obtained have indicated that Ag(111) exhibits no affinity for propylene carbonate at room temperature as monitored by work function $\Delta\phi$, measurements and Auger electron spectroscopy, AES. In contrast, sizable changes in $\Delta\phi$ were observed for similar experiments involving Ag(111) covered by K even when the latter was present at coverages well below a monolayer. The AES spectra of the K/Ag(111)-PC surfaces layer showed C, and O peaks indicating that the presence of K on the surface leads to an increase in the sticking coefficient of PC on Ag(111). A series of AES spectra recorded after such reacted layers were heated at different temperatures provided evidence that all the reaction products including K can be desorbed from the surface at about 600°C rendering a clean, highly ordered Ag(111) surface.

It may be concluded on the basis of the results obtained that highly reliable information regarding the reactivity of non-aqueous solvents with alkali metals can be obtained by the methods developed during the past two years of this research program. During the preparation of this final report the instrumental array involved in the thermal desorption spectroscopy measurements became fully operational and has provided much needed insight into the nature of the products generated by alkali metal-non aqueous solvent reactions.

VII. References

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VIII. Publications

1. Pilar Herrera-Fierro, D. A. Scherson and G. S. Chottiner, J. Vac. Technol. A5(4)646(1987)
2. Xue-kun Xing and D. Scherson, J. Electroanal. Chem., 216,261(1987)

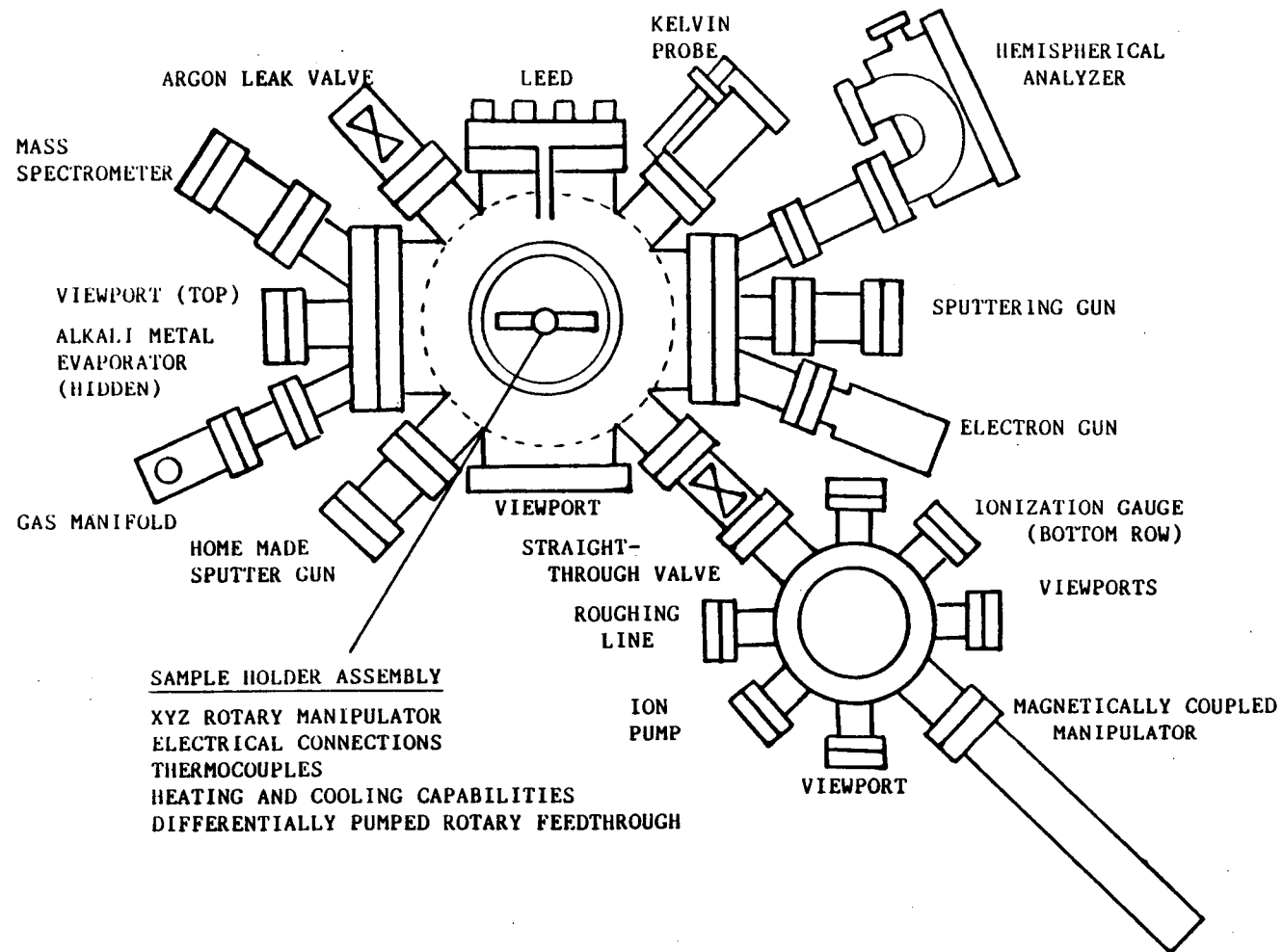


Fig. 1. Schematic diagram of the ultra high vacuum system in its present configuration. Inset: Manipulator-Cryostat. A. Cryostat, B. Four-way cross, C. Differentially pumped rotary feedthrough, D. XYZ manipulator, E. Copper main bar, F. Heating Assemblies, G. Samples and their mounting tabs, H. Sapphire-silver sandwich. (see page 13)

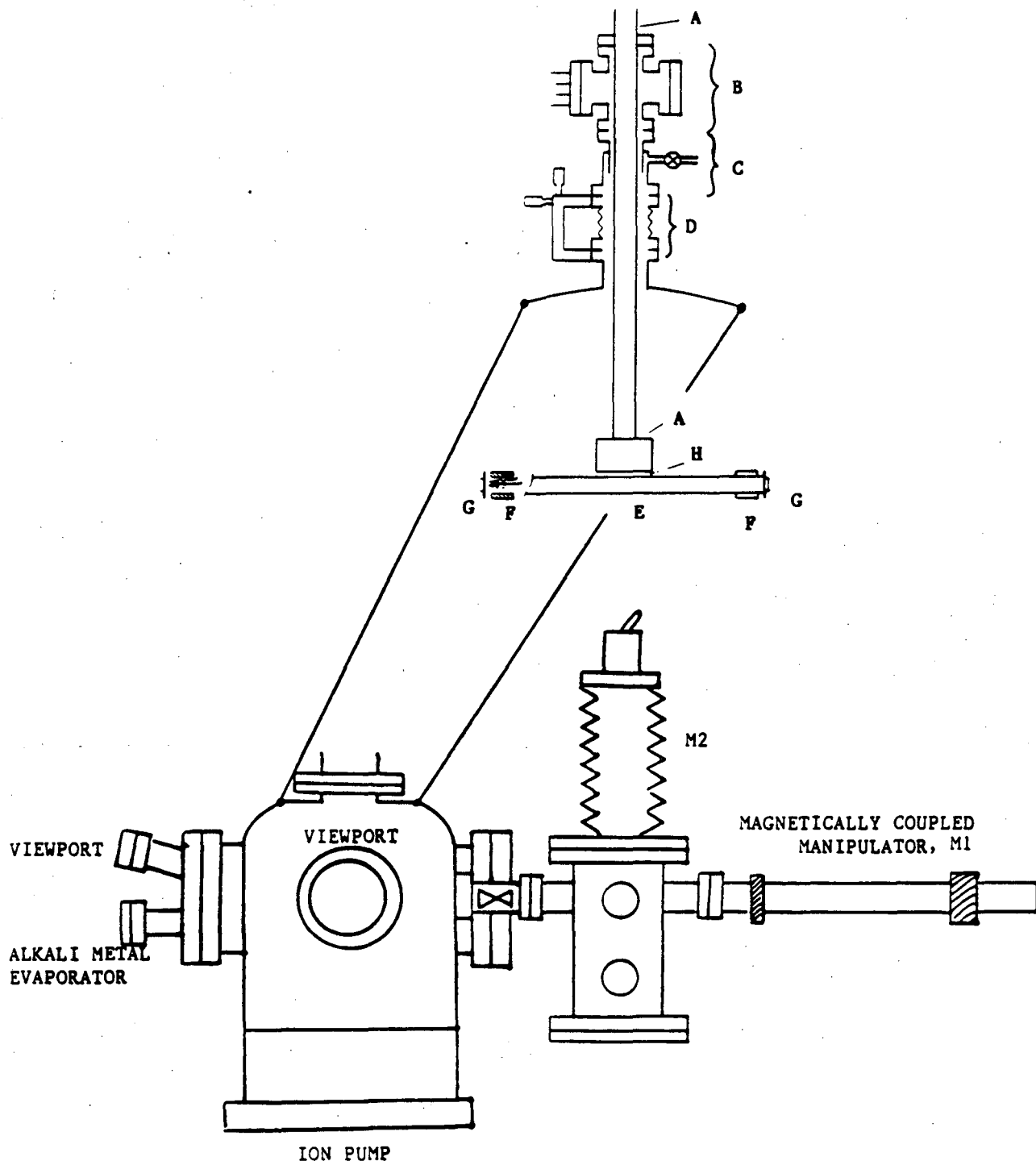


Fig. 1. Inset: Manipulator-Cryostat.

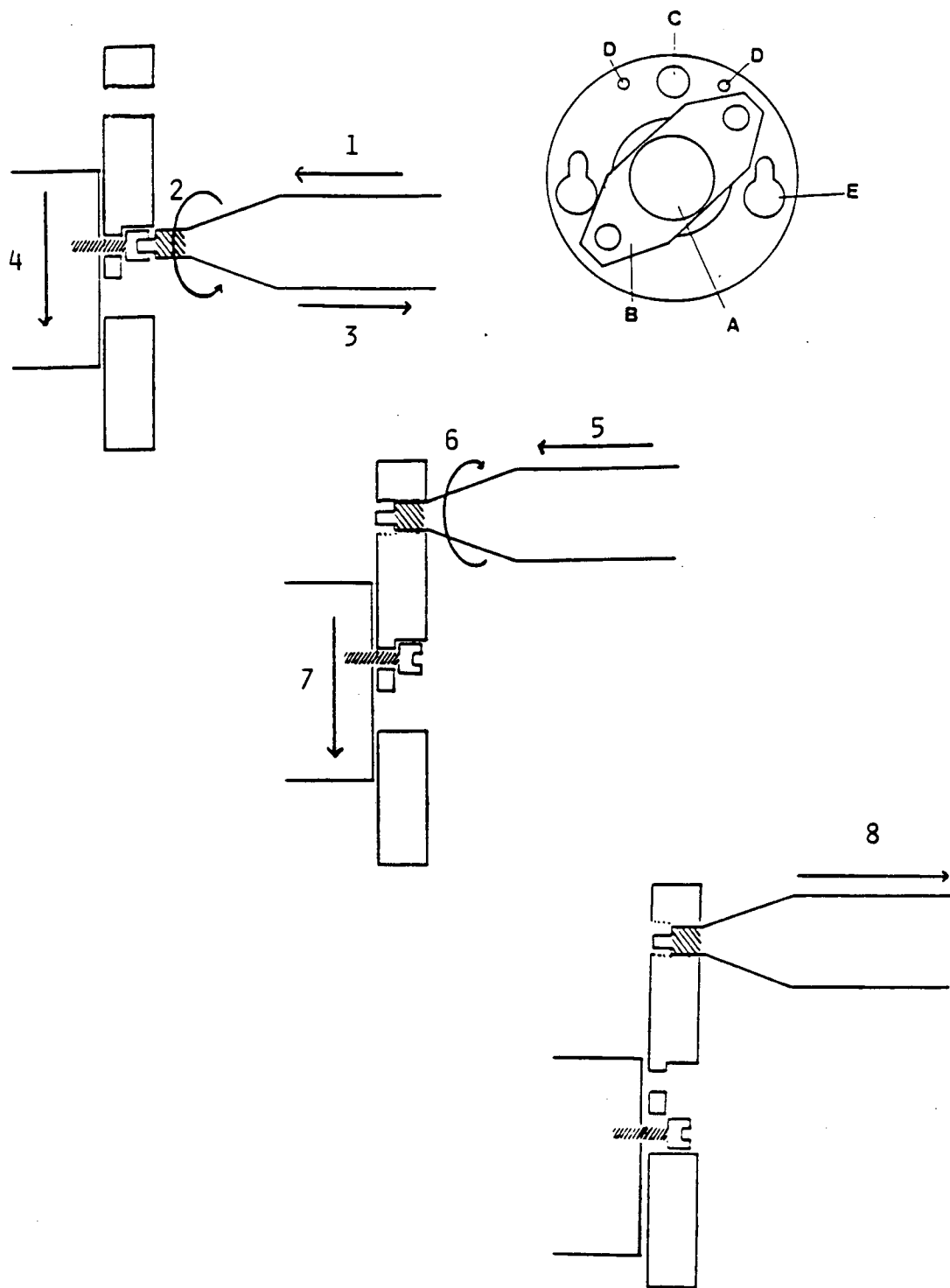


Fig. 2. Sample holder and transfer mechanism:
 A. Single crystal specimen, B. Metal strip, C. Threaded hole used for the transfer of specimens in and out of the main UHV chamber, D. Thermocouple wire holes, E. Slotted holes used for attaching the sample holder to either one of the two vertical manipulators. The numbers represent the sequence in which the operations associated with the transfer of specimens are performed.

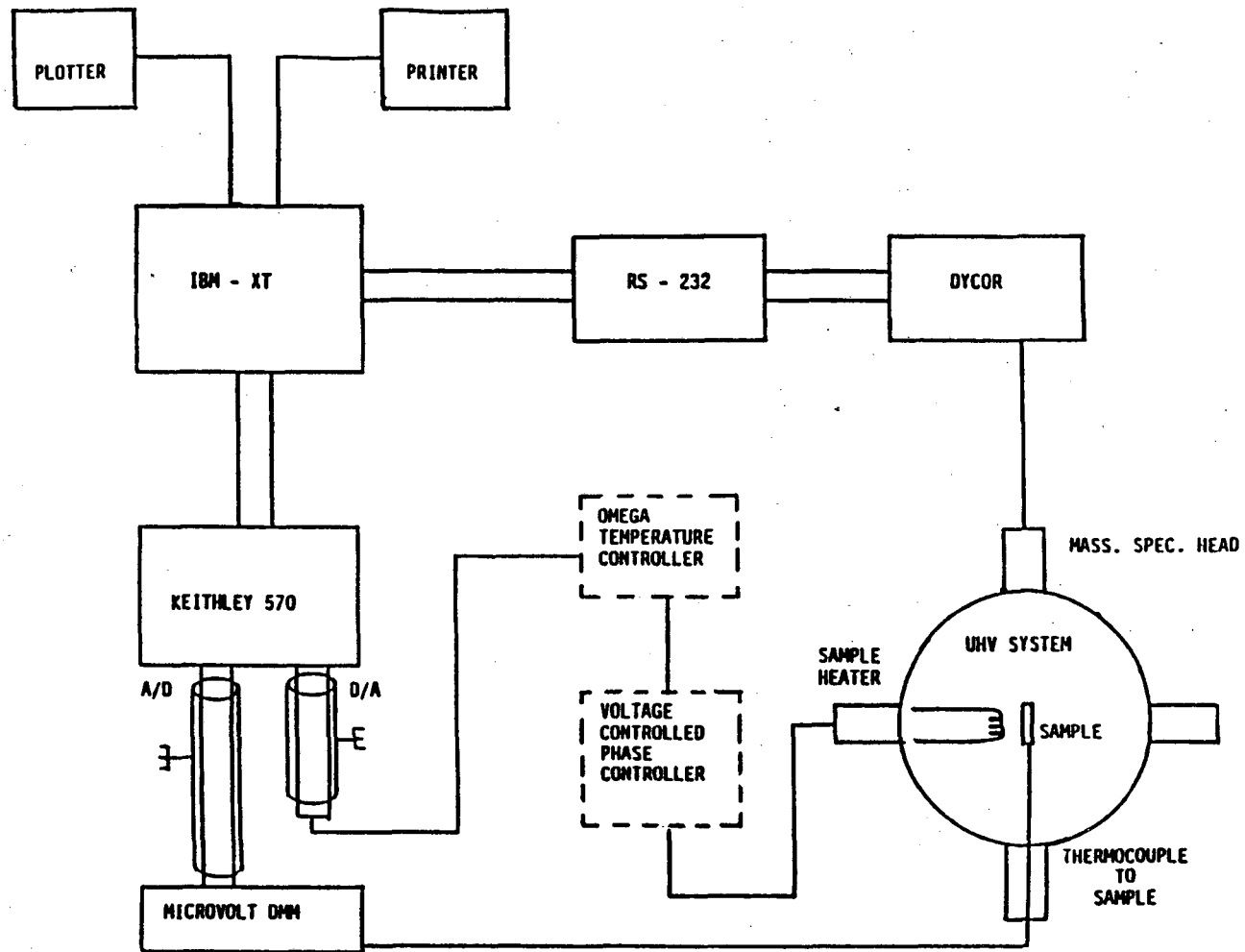


Fig. 3. Schematic diagram of thermal desorption system

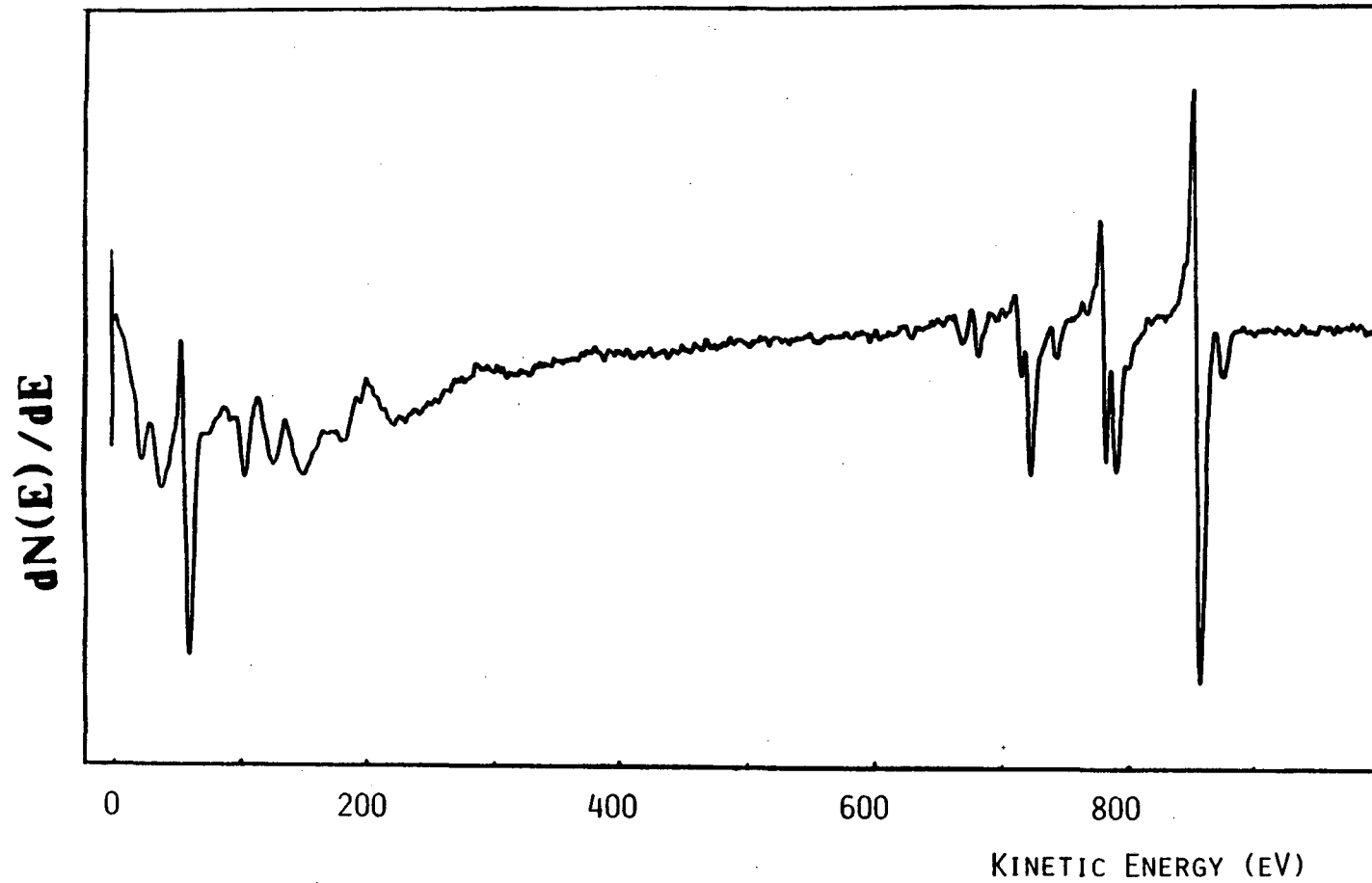


Fig. 4. Auger electron spectra of clean highly ordered Ni(111)

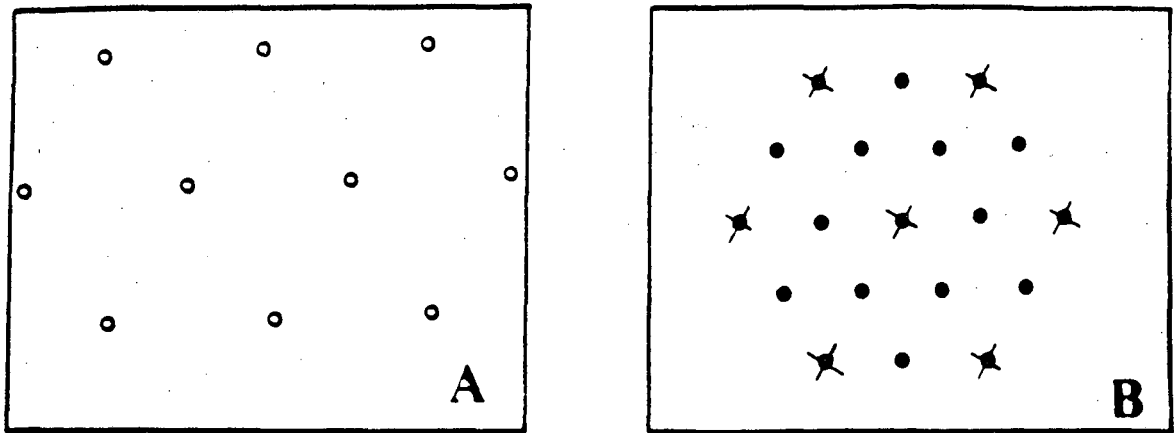


Fig. 5. Low energy electron diffraction pattern of O_2 adsorbed on Ni(111)

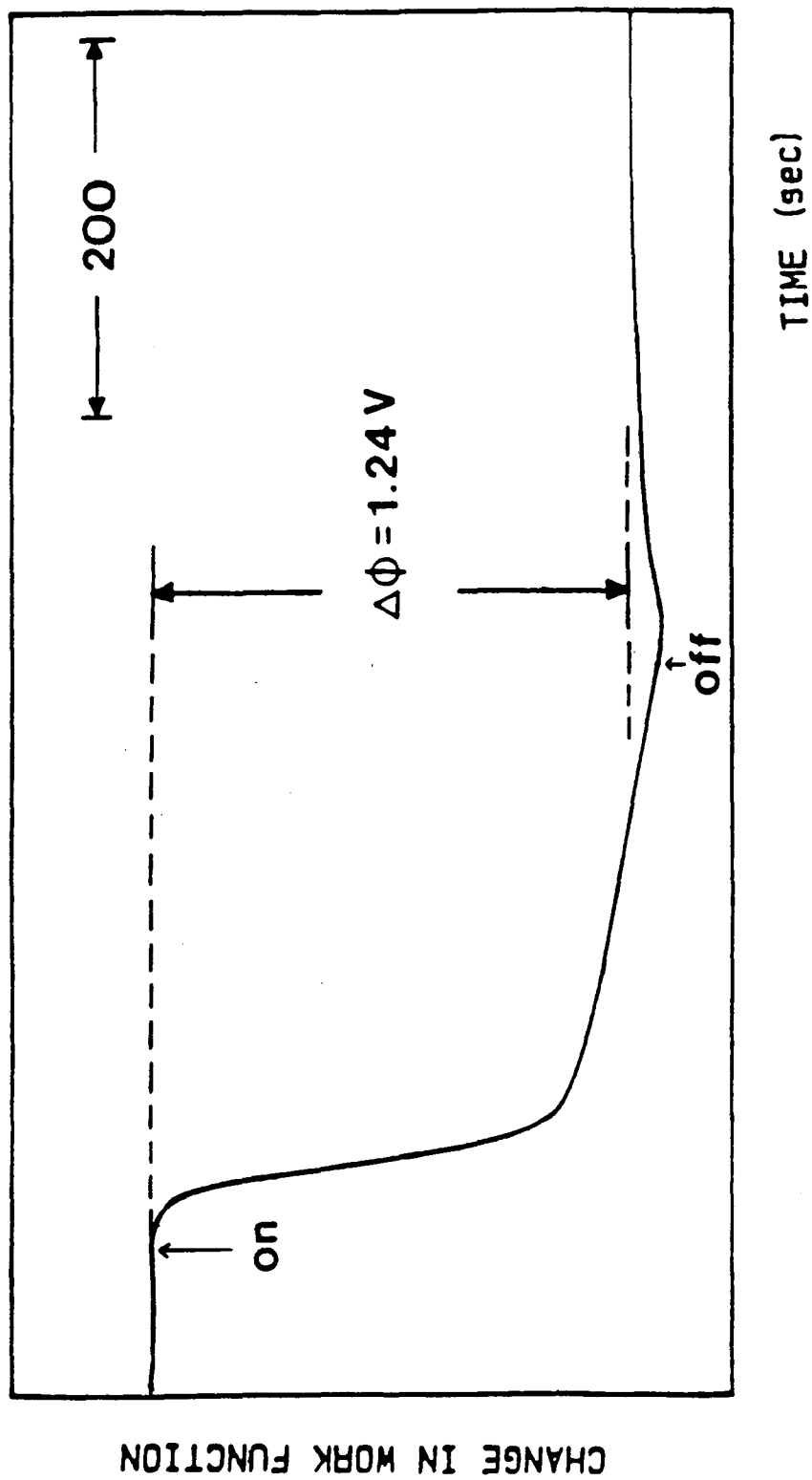


Fig. 6. $\Delta\phi$ vs. exposure time of Ni(111) to CO

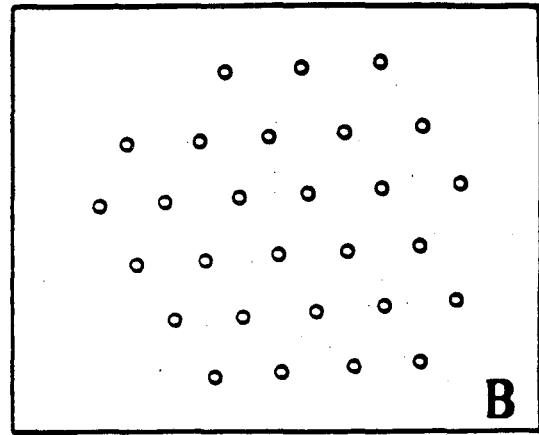
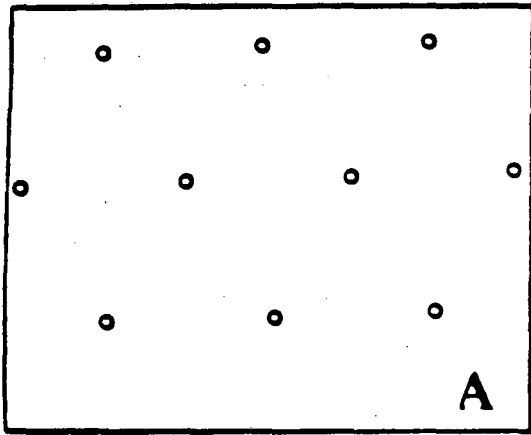


Fig. 7. Low energy electron diffraction patterns of A. Ni(111) and B. K adsorbed on Ni(111).

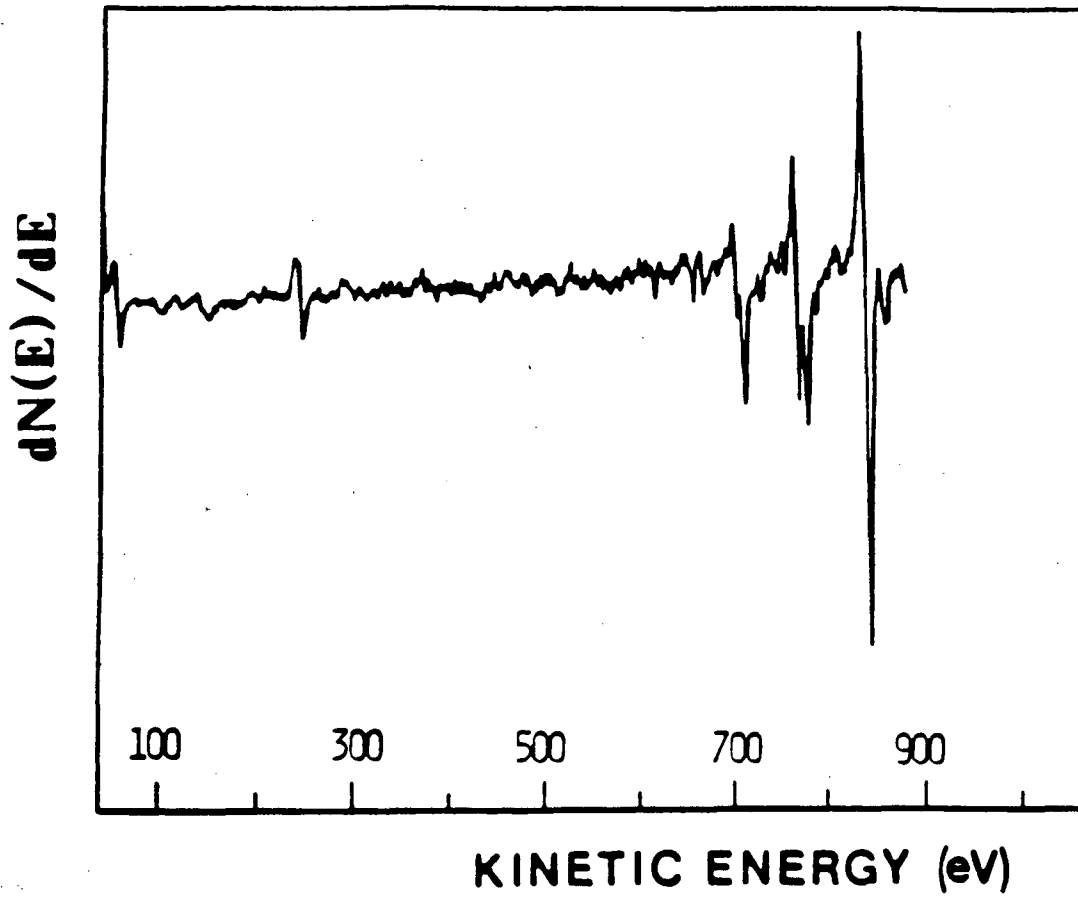


Fig. 8. Auger electron spectra of K adsorbed Ni(111)

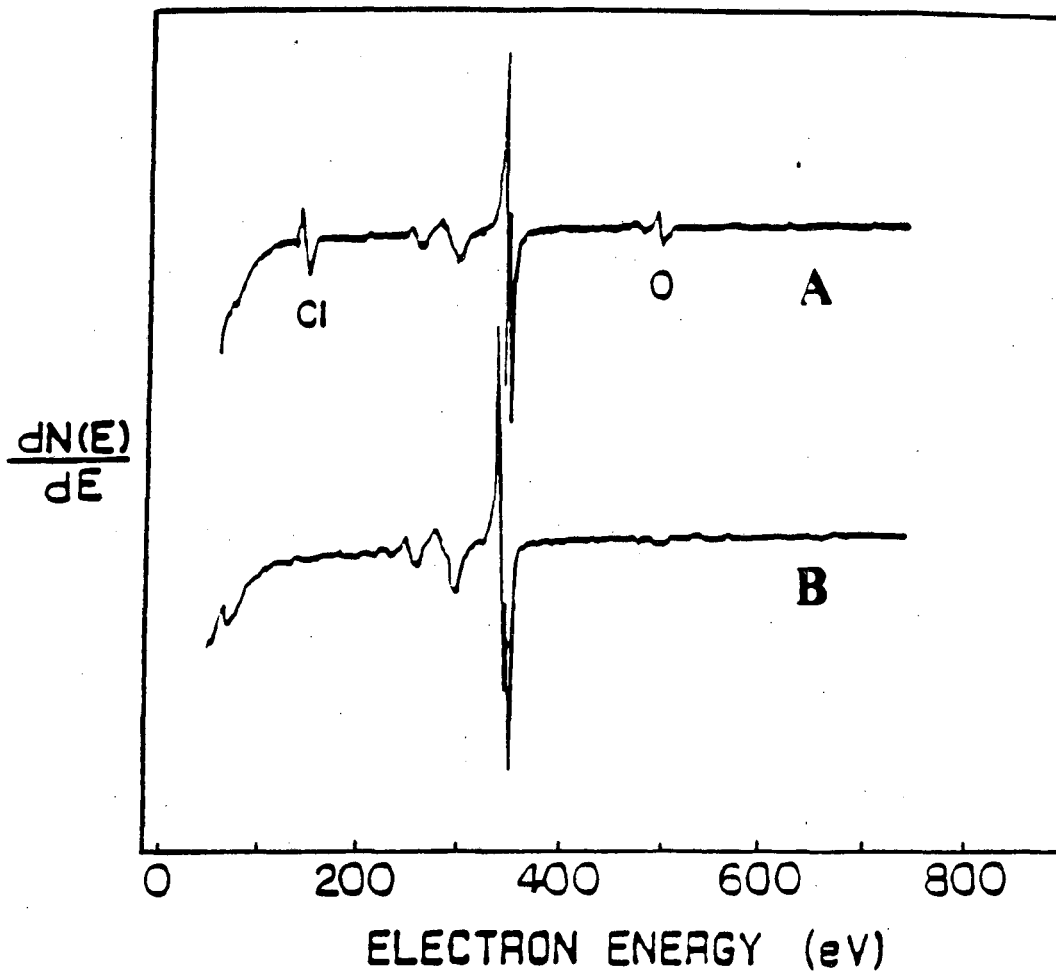


Fig. 9. Auger electron spectra of Ag(111), A before and B after cleaning

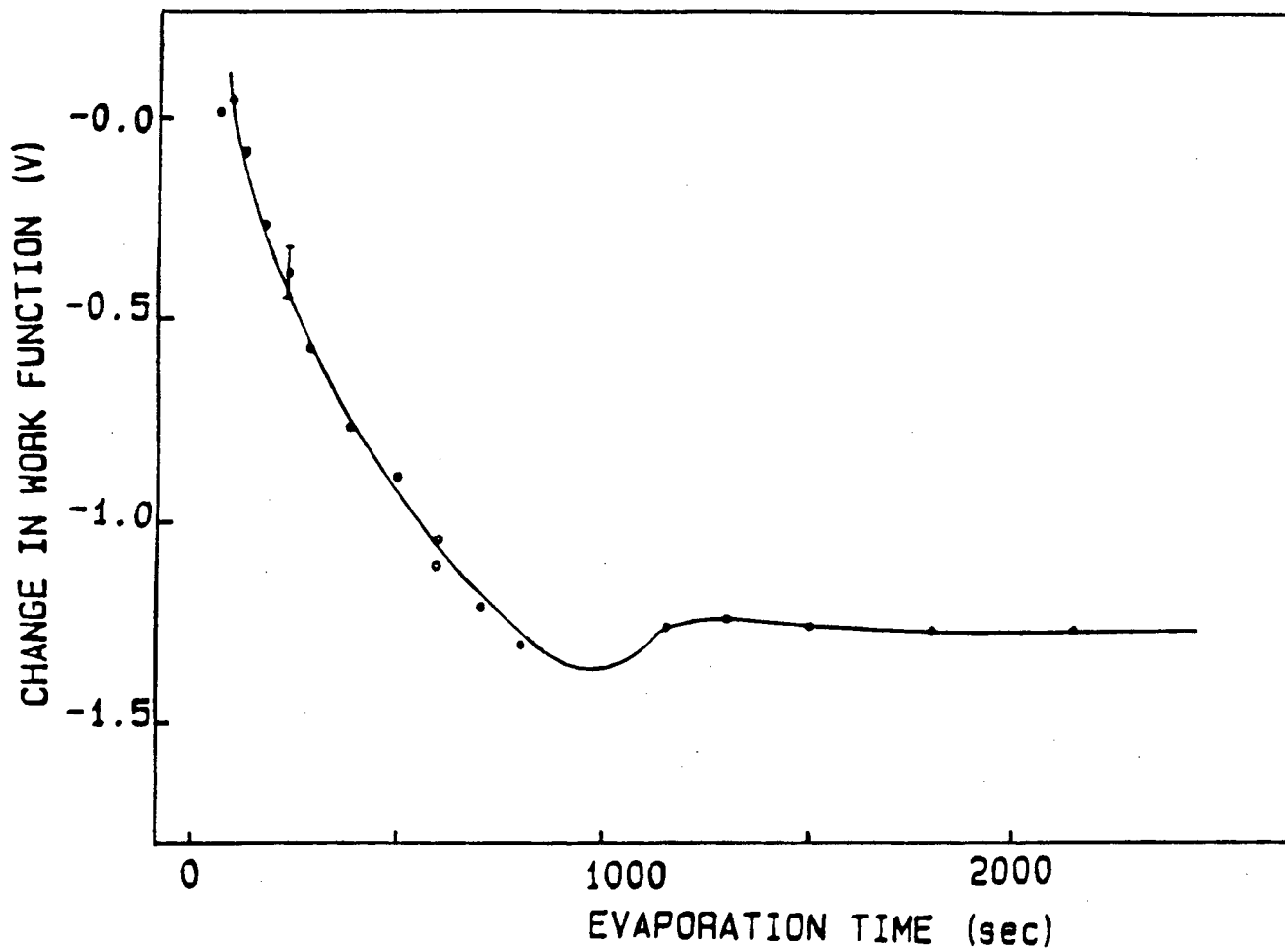


Fig. 10. $\Delta\phi$ vs. deposition time of K on Ag(111)

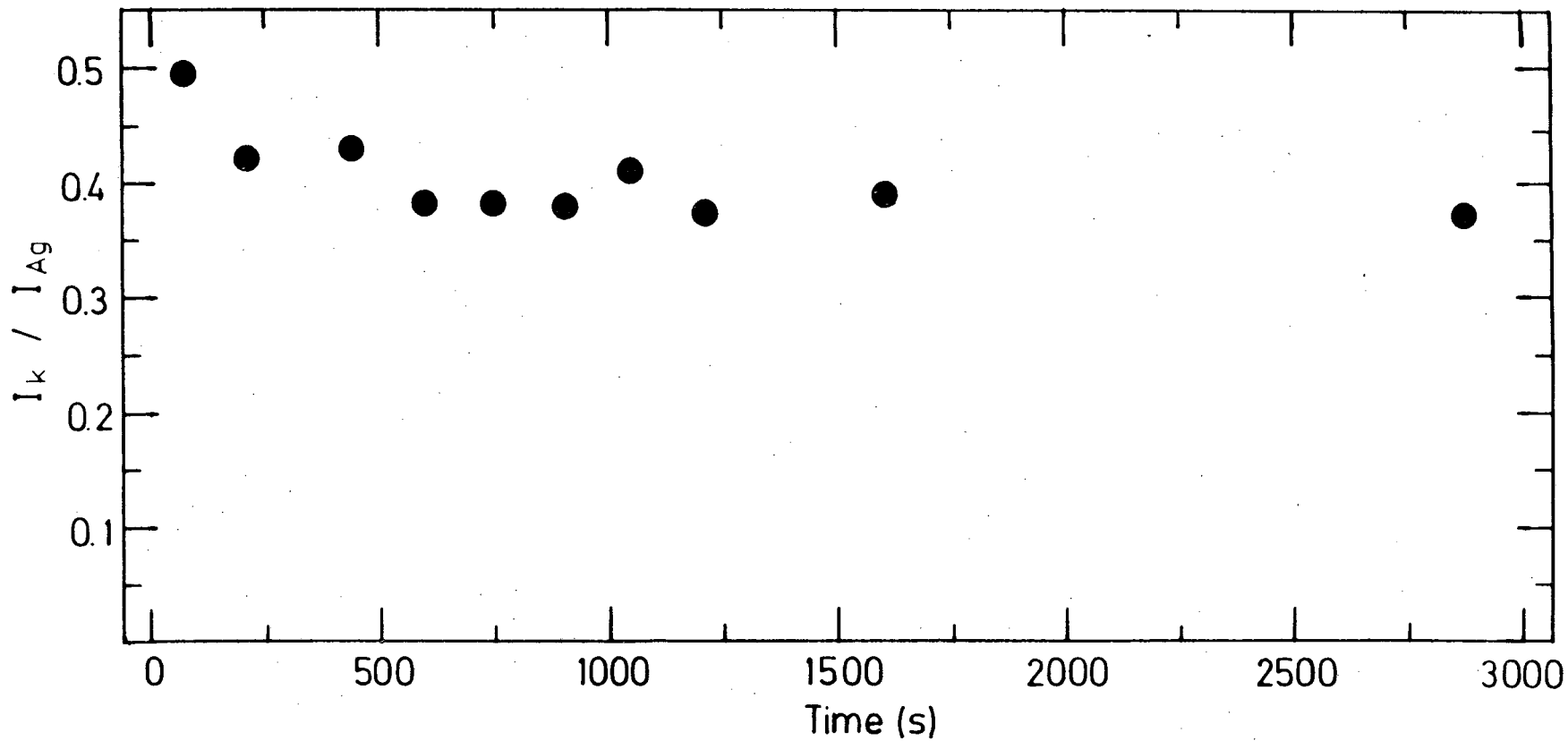


Fig. 11. K AES peak intensity as a function of exposure time to the electron beam

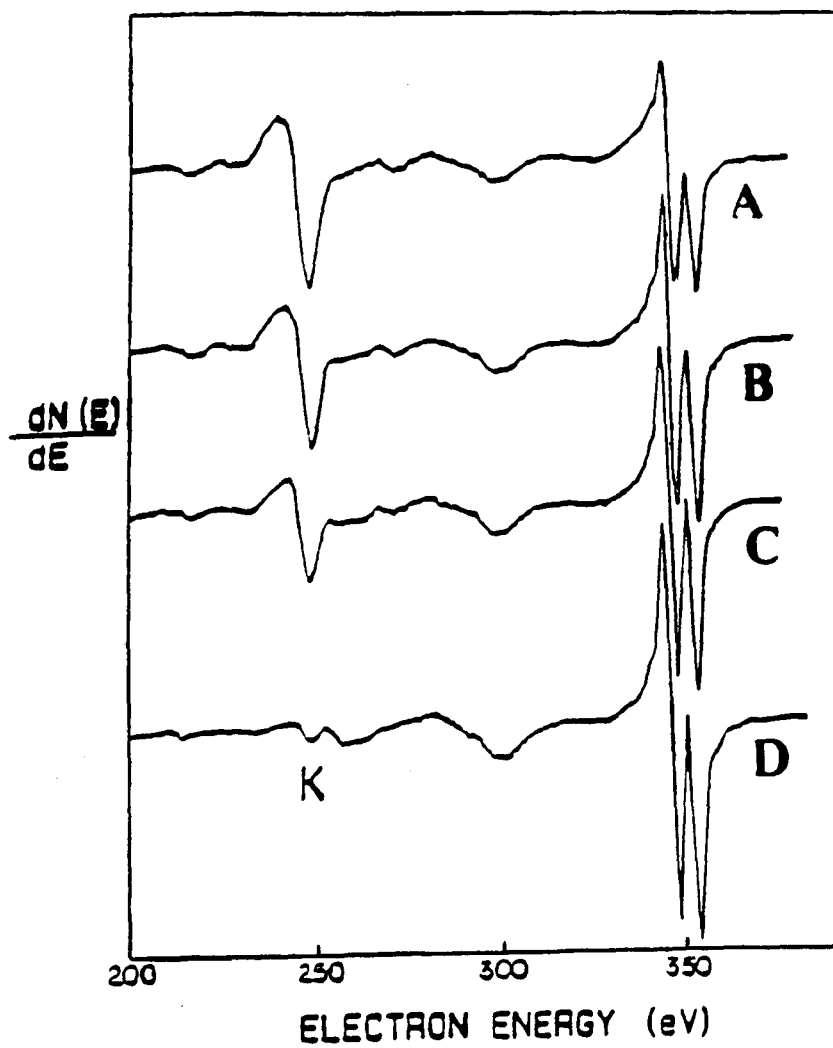


Fig. 12. AES spectra for different K coverages. A. 50%, B. 35%, C. 28%, D. 5%.

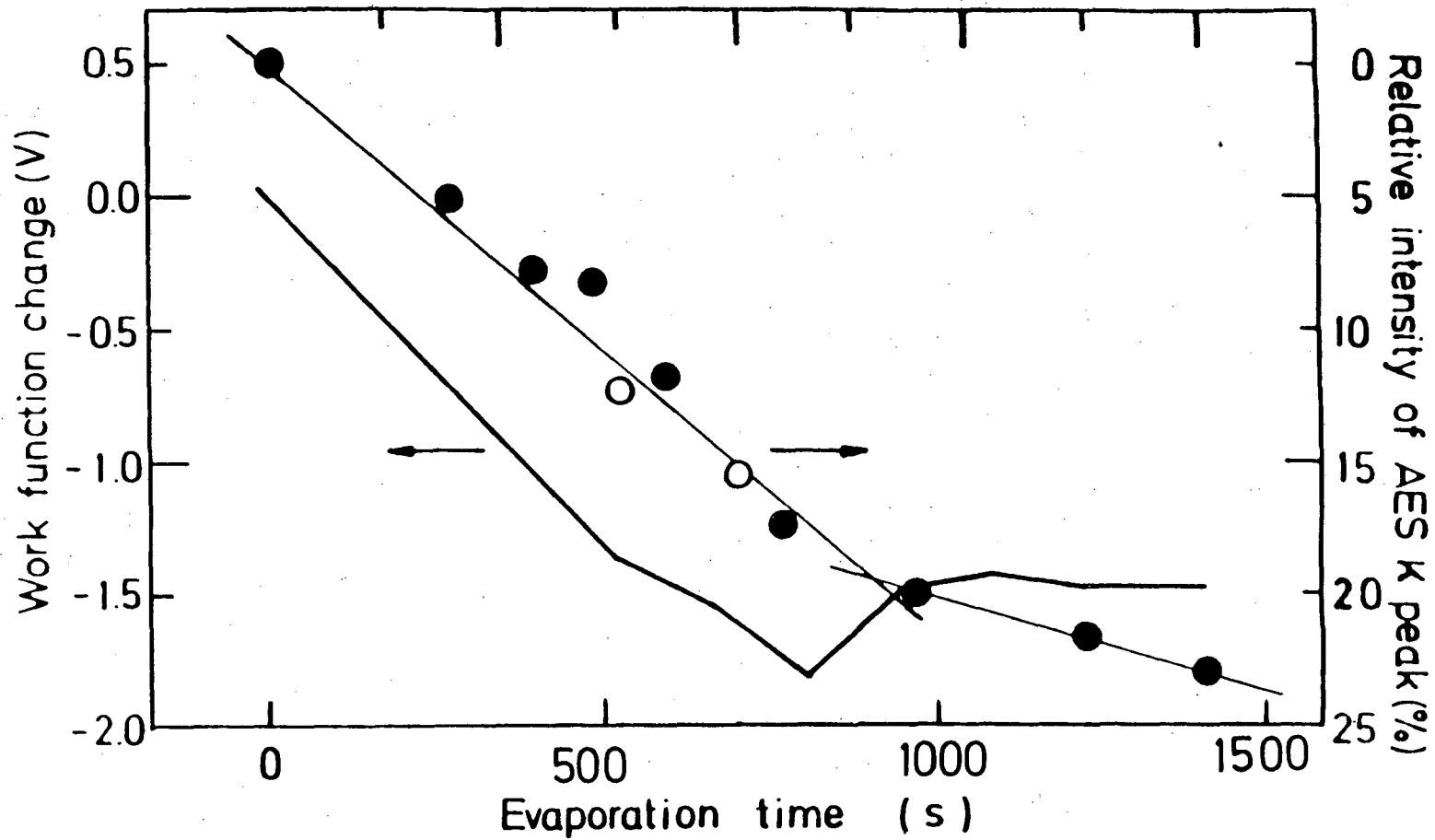


Fig. 13. Composite diagram of work function and K AES line intensity vs K deposition time

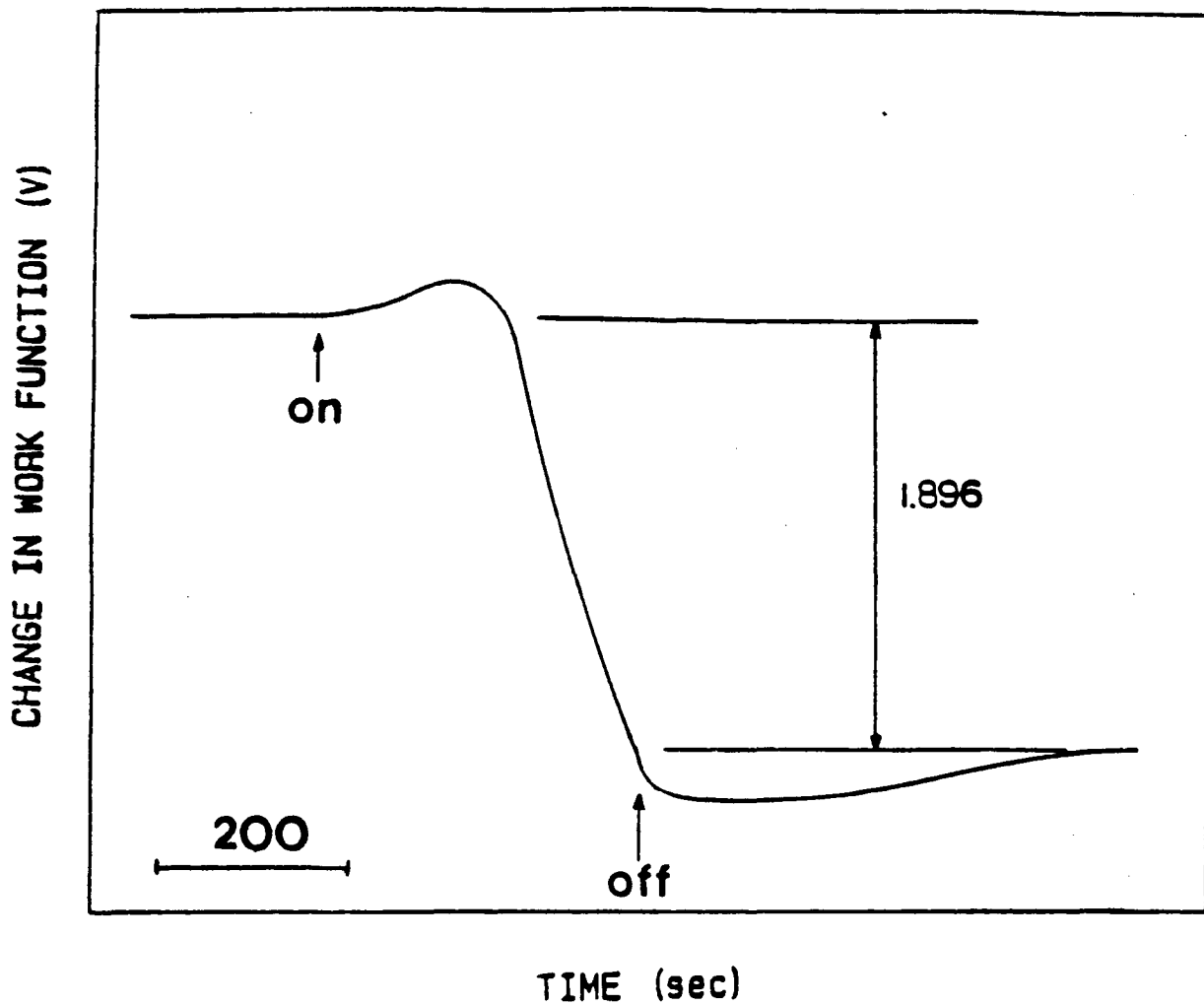


Fig. 14. $\Delta\phi$ of several monolayers of K adsorbed on Ag(111) as a function of exposure to propylene carbonate, PC.

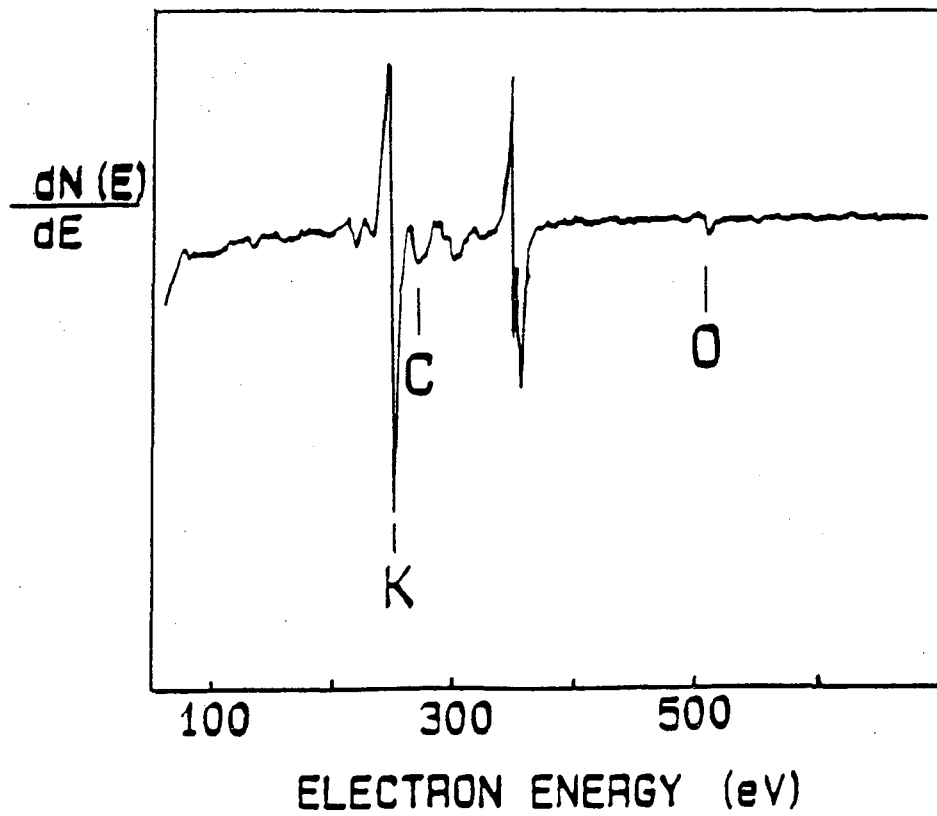


Fig. 15. AES spectra of surface in caption Fig. 14 after exposure to PC

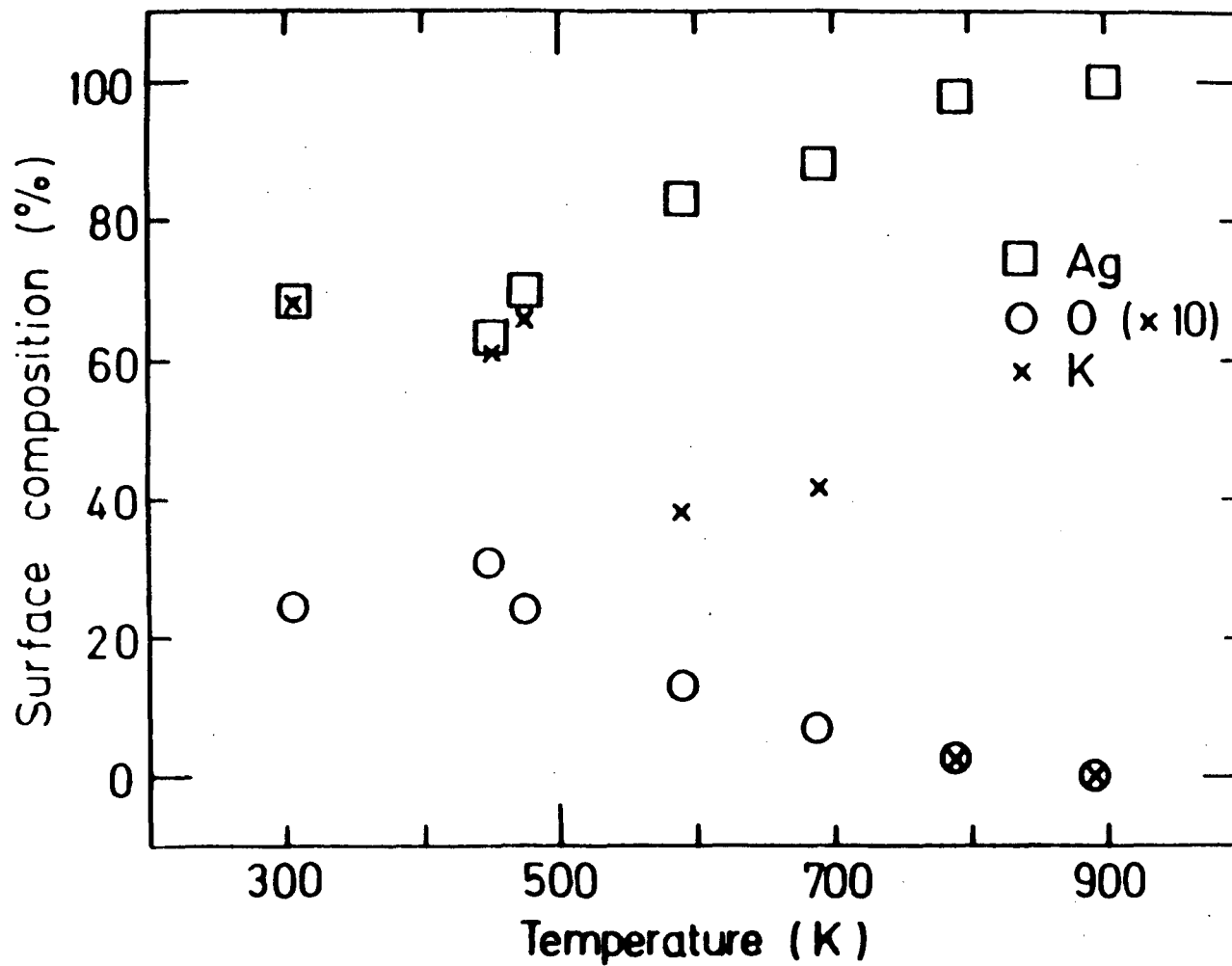


Fig. 16. Surface composition as evaluated from the AES peak intensities of K, O, and Ag as a function of substrate temperature of a synthetic PC layer on K/Ag(111) in caption Fig. 15

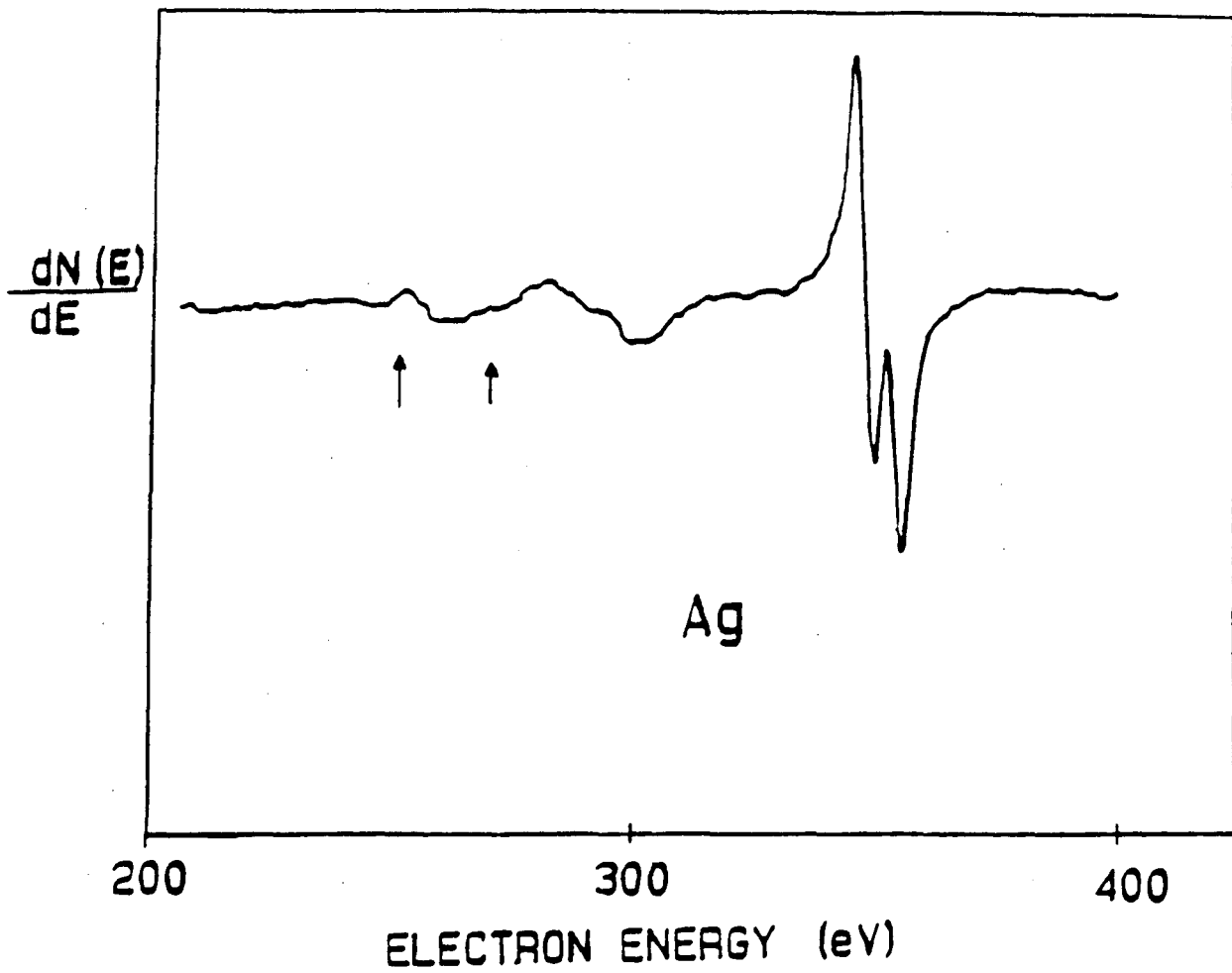


Fig. 17. AES spectra after heating surface in caption Fig. 16 to about 600°C.

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