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NOTE ON THE FIELD EMISSION MICROSCOPIC OBSERVATION OF DECOMPOSITION OF HYDRAZINE ON RHENIUM

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Field emission microscopic observation was conducted on emission patterns and the average work function of a rhenium surface at which hydrazine vapour was jetted. These measurements were carried out with an FEM cell communicating with an ultrahigh vacuum line and immersed in liquid nitrogen. Hydrazine was introduced into the cell from a reservoir at about 10^{-5}mm Hg pressure through a gas leak pointing at the rhenium tip which was preliminarily made sure of the clean surface. Patterns were observed in course of the introduction of hydrazine. The cell was now isolated from the reservoir and the tip was subjected to intermittent heat treatments without applying electric field at temperatures successively raised from 300° to 1000°C; each heat treatment was followed by a series of the measurements.

The results obtained are described in the following several stages of experiment. (1) In course of introduction of hydrazine at −195°C, only slightly different patterns from that of the clean rhenium surface were observed as seen from Plates 1 and 2, while the average work function, ϕ, as observed after the isolation of the cell, decreased by *ca.* 0.6 eV as shown in Fig. 1. (2) Heat treatments of the tip, beginning at 300°C, caused remarkable changes in pattern (Plate 3) and a further decrease of ϕ by *ca.* 0.1 eV at around 400°C. (3) Successive heat treatments at from *ca.* 400°C to 500°C gave rise to subsequent conspicuous changes of the pattern (Plate 4) and a distinct increase of ϕ (Fig. 1). (4) The ϕ continued to increase along with successive heat treatments to attain a maximum value, *ca.* 0.5 eV above that of the clean surface, when the tip was heat treated at 600°~700°C (Fig. 1 and Plate 5). (5) The heat treatments at about 1000°C recovered the pattern (Plates 6 and 1) and the ϕ value of the clean surface. These stages are illustrated in Fig. 1.

From these observation we might conclude as follows. The initial decrease

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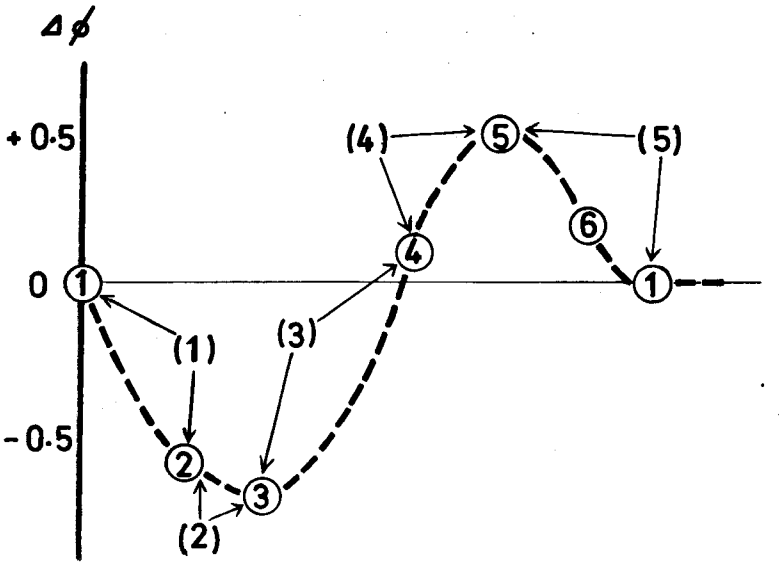

Fig. 1. Changes of ϕ of the rhenium surface treated with hydrazine.

Parenthiesized numerals in the Figure refer to the following stages, respectively; (1) the introduction of hydrazine at −195°C, (2) intermittent heat treatments of the tip at temperatures from *ca.* 300° to 400°C, (3) those from *ca.* 400° to 500°C, (4) those from *ca.* 500° to 700°C, and (5) those from *ca.* 700° to 1000°C. Encircled numerals refer to the Plates of patterns.

of ϕ in stages (1) and (2) is due to the dipoles of physisorbed hydrazine, N_2H_4(a), and chemisorbed radicals, NH_2(a) and/or NH(a), with their positive poles directed away from the rhenium surface[1]. The increase of ϕ in stages (3) and (4) is attributed to adsorbed hydrogen atoms, H(a), slightly negatively charged[2] and perhaps adsorbed nitrogen atoms, N(a)[1]. The later decrease of ϕ, in stage (5), is ascribed to the desorption of H(a) and N(a). It is inferred from the recovery of the ϕ value and the pattern of the clean surface by the heat treatments at around 1000°C that adsorbed species are desorbed completely from the rhenium surface.

References

1) K. AZUMA, This Journal, **9**, 55 (1961).
2) T. TOYA, *ibid.*, **8**, 209 (1960).

Plate 1

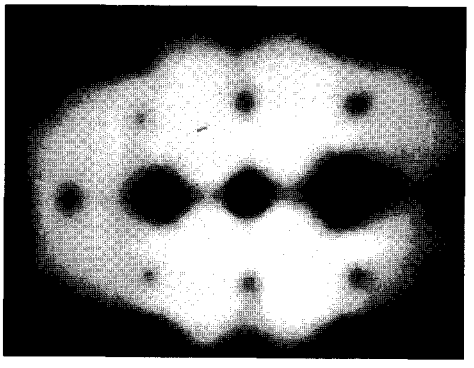

Plate 2

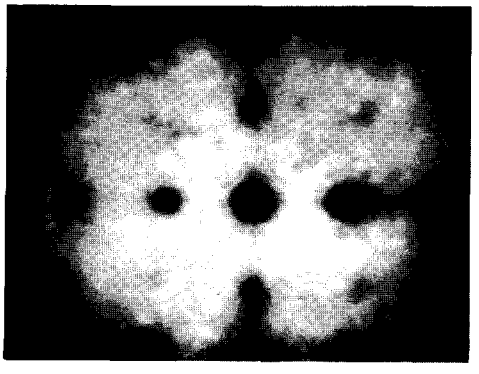

Plate 3

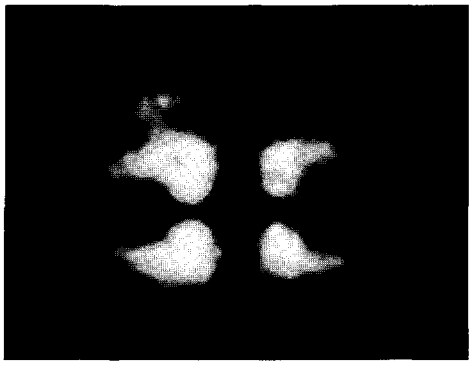

Plate 4

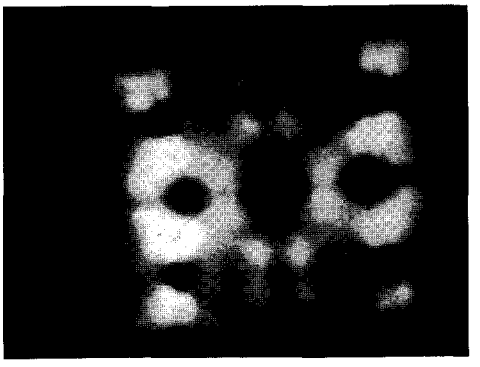

Plate 5

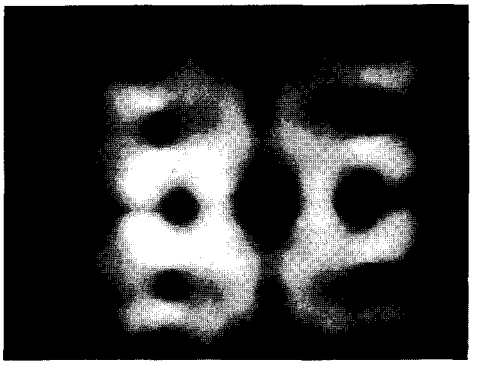

Plate 6