NUCLEATION AND CRYSTAL GROWTH OF Cu ON Ir TIPS UNDER ULTRA-HIGH VACUUM AND IN THE PRESENCE OF OXYGEN

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Results concerning the morphology of Cu adsorption layers deposited from vapor under ultra-high vacuum on Ir tip and the influence of oxygen on this morphology are reported. The method employed was field electron emission microscopy. It was found that the presence of oxygen decreases the copper wettability of iridium. Preadsorption of oxygen on the Ir surface is followed by an increase in cohesion interaction between atoms of the Cu deposited onto the tip at room temperature. Coadsorption of Cu and O on the Ir tip surface at liquid nitrogen temperature, when followed by gradually heating the adlayer, results in crystallization of the deposit in the temperature range from 430 K to about 700 K. Some evidence indicates the formation of Cu_2O with a high degree of crystallinity under these conditions. Cu and O coadsorption on the Ir surface at a temperature higher than 1090 K leads to selective accumulation of Cu on the {111} faces and to formation of epitaxial crystals which are oriented to the substrate in the same manner as the Cu crystals grown at ultra-high vacuum from Cu flux containing no oxygen. Oxygen incorporated into the Cu beam interact preferentially with {011} and {001} Ir faces, where it can produce oxide layers.

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1. Introduction

Studies on metal/metal adsorption systems are stimulated by both pure scientific interest in the phenomena which accompany adsorption on metal surfaces as well as the suitability of such systems for practical applications. An ongrowing interest in bimetallic catalysts because of their proved selectivity over earlier catalysts containing clusters of a single metal [1] is a good illustration of the second incentive. Detailed studies of the metal/metal adsorption systems can provide important information about the electronic and atomic structures of the surface of

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bimetallic catalysts [2]. Many physical and chemical properties of an adsorption layer depend on its morphology and topography, these in turn are determined by deposition conditions. The present paper concerns investigation of an effect of oxygen on the process of nucleation and epitaxial growth of Cu nanocrystals on Ir with special attention paid to the influence of oxygen on the modes of growth and the crystallinity of the adlayer as well as the possibility of copper oxide formation. Cu adsorption on transition metals, particularly on W was studied intensively [3–12]. Other investigation's results on the nucleation and growth of copper crystals on an iridium surface are not known to the authors. Reported was, however, a study of work function variation and the course of submonolayer adsorption in the Cu/Ir system [13].

Field electron emission microscopy (FEM) is particularly useful for studying morphology of metal adsorption layers on metal substrates [14–17]. The use of thermally cleaned field emission tips as substrates provides surfaces with large low-index facets and terraces separated by atomic steps. On such surfaces, microscopic details of nucleation can be observed directly, with the resolution which does not exceed 2 nm, and under well-controlled experimental conditions. FEM enables one also to observe mobility of the adsorbate at various substrate temperatures.

2. Experimental

Investigations were carried out in a field electron emission microscope operated at liquid nitrogen temperature under ultra-high vacuum (the background pressure lower than 2×10^{-10} Torr). Ir tips, made from 0.1 mm diameter wire by electropolishing in 40% water solution of CrO_3, were spot welded to 0.2 mm diameter Mo heating loop. Prior to the Cu deposition the Ir substrate was cleaned for several hours by heating in an atmosphere of 10^{-8} Torr oxygen, at a temperature of 1500 K. Then the sample was heated to approximately 750 K under ultra-high vacuum (UHV) conditions. Immediately before the measurement the sample was heated by manifold flashes in excess of 2500 K. Changes of the tip temperature were estimated from the measurement of the electric resistance of the loop segment to which the tip was spot welded. For calibration, the loop resistance was measured at liquid nitrogen temperature and at room temperature. For the high temperature heating, when the loop was burning, the temperature of the tip was measured using an optical pyrometer.

A cone shaped coil, made from 0.4 mm diameter W wire, was heated up to 2000 K in a high vacuum for several hours before filling up with Cu. The evaporator was positioned below the FEM tip and Cu atoms impinged onto the bottom tip region from the direction perpendicular to the tip axis. During the operation the current feedthroughs of the evaporator were cooled down to liquid nitrogen temperature. Oxygen was admitted into the microscope system via a high precision dosage valve. Coadsorption of O and Cu was realized in such a way that the Cu source was heated for a short time in the presence of about 10^{-8} Torr oxygen and with the Cu source kept considerably below the temperature of Cu deposition. It was expected that atomic oxygen preadsorbed on the elements of the Cu source, would be captured by the vapor stream of the deposited copper.

Under these circumstances the current feedthroughs of the evaporator were not cooled.

Surface mobility of Cu on Ir was examined qualitatively. Relatively small doses of Cu diffused over the clean Ir surface with a very faint boundary of increased brightness in the FEM image. Diffusion of larger doses was characterized by an advancing sharp diffusion front. The first type of surface mobility of adsorbate is usually associated with sub-monolayer diffusion, the second one with the diffusion of a multilayer [15, 16]. The mobility of Cu on the Ir surface was investigated because in metal/metal adsorption systems the stage of the nucleation process, that leads to the crystal growth, usually occurs in a temperature range for which the diffusion with its sharp moving front is observed [17].

3. Results and discussion

3.1. Cu adsorption, diffusion, and nucleation on clean Ir under UHV

Typical stages of Cu diffusion over the surface of an Ir crystal are shown in Fig. 1. Large enough to be spread with a sharp advancing boundary, doses of Cu were deposited under UHV onto the clean Ir substrate (Fig. 1a), which was kept at liquid nitrogen temperature. Due to a lower work function, the area of the tip covered with Cu was visible on the screen as a region of enhanced electron emission (Fig. 1b). While increasing the tip temperature up to about 600 K, the deposit started to diffuse over the tip surface. It was found that Cu migrates especially easily over {131} facets and the terraces surrounding these facets, along the ⟨011⟩ direction (as it is indicated by arrows in Fig. 1c). Diffusion into the (001) Ir plane vicinity and over this plane was energetically most difficult and required higher temperatures. At this stage of diffusion, the diffusion front had formed a circle around the central (001) plane of Ir (Fig. 1d) and moved toward the center of this plane. Since the diffusion front had reached the edges of the central (001) facet of iridium, nucleation events began to occur in the area which still was not covered by the diffusing Cu layer. A four of such Cu nuclei are visible on the central (001) plane in Fig. 1d. They became larger and brighter during the progress of diffusion and coalesced with the advancing adlayer of copper migrating toward the center of (001) plane. The nuclei disappeared when the entire tip was covered by Cu layer. Diffusion experiment was performed both in the presence of the imaging field and under field-free conditions. No influence of the electric field on the nucleation events described above was noticed. This type of nucleation has not been observed in the FEM studies of Cu adsorption on bcc tungsten [3–8]. The influence of gaseous impurities, coadsorbed with the material during deposition, on the initiation of this type of nucleation, although probable, should be rather excluded due to good vacuum conditions and relatively low temperature of evaporator. A conciliation of the phenomena observed during both the diffusion and the direct deposition required the assumption that adhesion and cohesion forces in the Cu/(001)Ir adsorption system depend on Cu coverage and for coverages from the range between a fraction of monolayer and a monolayer the cohesion forces prevail. That means that for this range of coverage the Volmer–Weber (V–W) mechanism of nucleation should be suggested. The reduced Cu diffusion rate onto
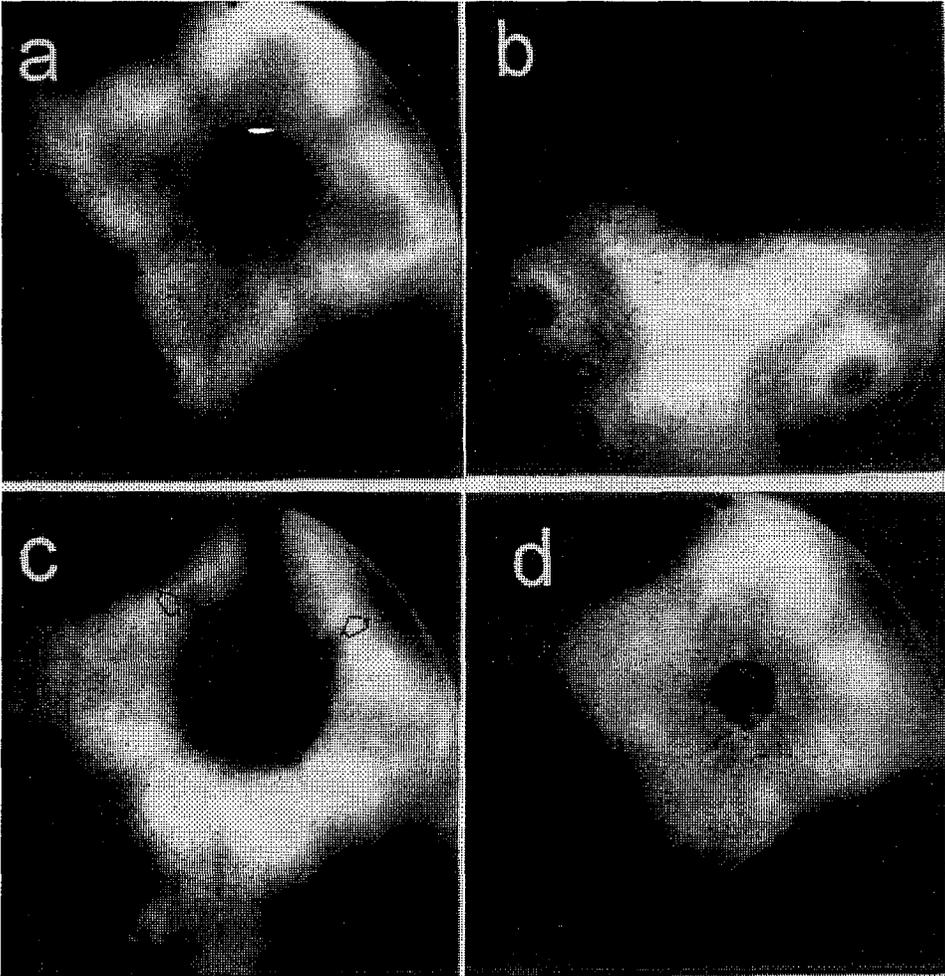
Fig. 1.   Adsorption stages of Cu on a surface of Ir tip: (a) FEM pattern of the substrate
prior to Cu deposition. (b) After Cu deposition onto Ir tip at liquid nitrogen temperature.
The deposit of copper, owing to its much lower work function, is imaged as the bright
area of the tip at the lower part of the photograph. (c) A stage of spreading of the bright
area over Ir surface via diffusion with an advancing sharp boundary. The arrows indicate
the directions of diffusion. (d) Diffusion front surrounds the (001) Ir face together with
a four of three-dimensional Cu nuclei formed on his face.

the (001) Ir plane from the surrounding stepped region indicates, like in the case
of the Cr/(001)W system [18], the existence of a diffusion barrier at the steps of
the (001) Ir terraces. A diffusion barrier on the steps does not limit the mobility
of Cu atoms over the (001) plane or (001) terraces, it reduces only the amount of
adsorbate transported through the steps. The energetics of such diffusion creates
virtual conditions of proper coverage for the V–W nucleation, which cannot be
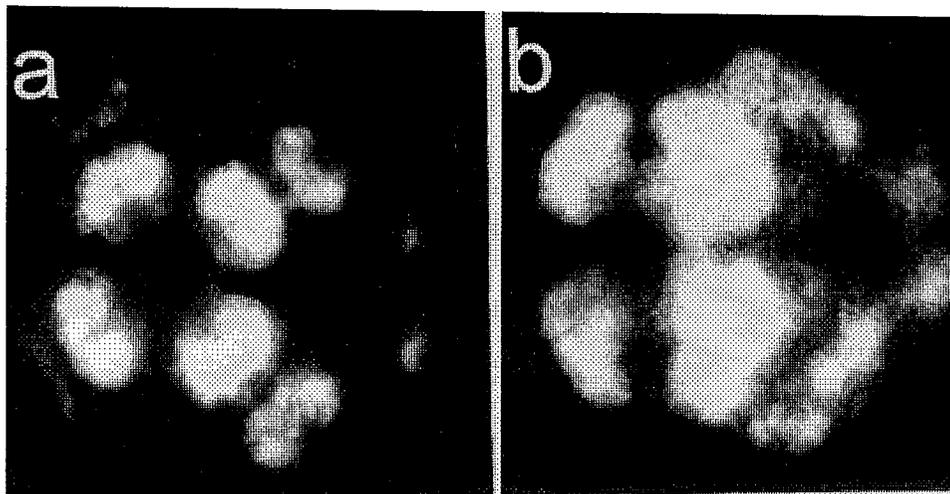achieved during the direct deposition on a hot surface.

Fig. 2. Cu epitaxial crystals of a high degree of perfection formed on the Ir tip as a result of coalescence of a few Cu crystallites. FEM patterns of: (a) Ir tip of the curvature radius $r_{Ir} = 110$ nm; (b) the Cu epitaxial crystal of curvature radius $r_{Cu} = 70$ nm.

When Cu was deposited under UHV onto the substrate at temperatures from the same range where the multilayer diffusion occurred (between 600 and 800 K), the nucleation of three-dimensional Cu crystallites generally followed the Stranski–Krastanov (S–K) mechanism. The nuclei were observed only on the substrate precovered by Cu, with the density of the nuclei number decreasing with increasing substrate temperature during deposition. This remains consistent with the nucleation pattern of numerous metal/metal systems studied by means of FEM [4]. Larger crystallites nucleated on the edges of {111} Ir planes. Epitaxial crystals of Cu with the epitaxial relationship {111} Cu ∥ {111} Ir with ⟨011⟩ Cu ∥ ⟨011⟩ Ir were formed as a result of coalescence of a few Cu crystallites after heating the deposit above 1100 K. An example of such a crystal is shown in Fig. 2.

3.2. O_2 adsorption and iridium oxide formation on Ir

The adsorption of oxygen on the Ir tip held at room temperature is accompanied by increasing the average work function, as measured by the Fowler–Nordheim method [15]. A plot of this variation as a function of exposure to oxygen is presented in Fig. 3. The work function increases monotonically and approaches a value of about 6.6 eV. FEM patterns of the successive adsorption stages rather do not reveal marked changes in the topography of the tip surface. The formation process of an IrO_x layer is illustrated in Fig. 4a–d. The figure shows a sequence of microscopic patterns, which were obtained as a result of heating the tip after the adsorption of oxygen at room temperature (exposure about 3 L). A pattern of the clean tip surface is shown in Fig. 4a. If one assumes the average work function of the clean Ir to be 4.87 eV [19], then the average work function of the Ir tip upon the 3 L exposure rises to the value of 6.6 eV. Heating the tip to 950 K for a few seconds results in a further increase in the average work function to 6.8 eV and
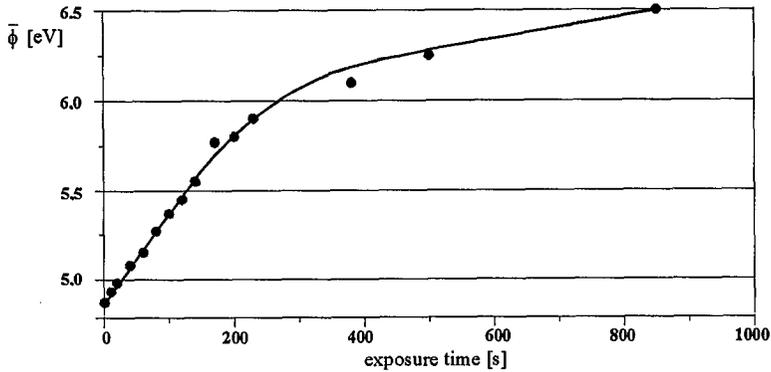
Fig. 3.   Changes of the average work function caused by O_2 adsorption on Ir tip.
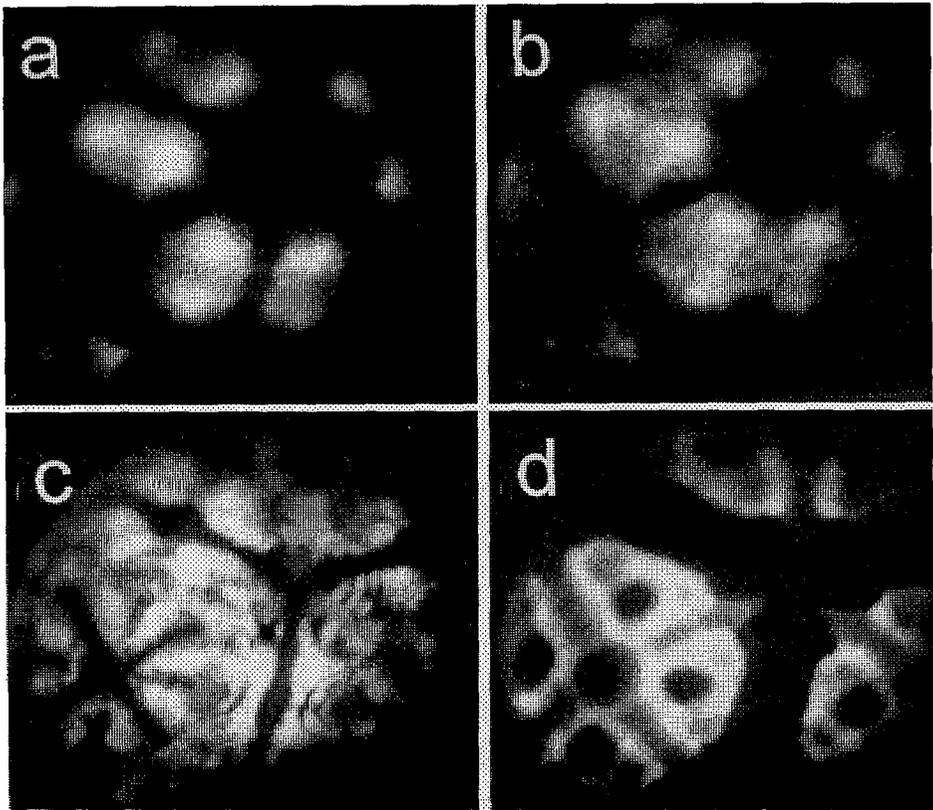

Fig. 4.   Oxygen adsorption and iridium oxide formation on Ir tip. (a) The clean substrate surface; (b) FEM pattern of the same tip after 3 L exposure to oxygen at room temperature and the heating up to 950 K — the beginning of the oxide formation. (c) FEM pattern of the IrO_x oxide formed after further heating up to 1390 K. (d) FEM pattern of a more ordered oxide species obtained after a short temperature flash up to 2350 K.

starts changes in surface topography (Fig. 4b), which bring about the formation of an oxide layer of IrO_x (Fig. 4c) and lowering of the work function to 6.3 eV. The layer IrO_x is formed in the temperature range of 1320–1390 K. A further heating leads to the gradual decrease in the work function. Figure 4d shows the tip surface after heating to 2350 K. The work function has decreased to 5.6 eV and the oxide layer shows more order on the {001} faces of Ir and their vicinity. A high temperature flashing over 2500 K finally leads to the recovery of the clean Ir tip surface.

3.3. Cu adsorption on Ir precovered by O and coadsorption of Cu and O on Ir

The presence of oxygen on the Ir tip during Cu deposition changes the nucleation mechanisms. The room temperature deposition of small Cu doses (submonolayer coverages) onto the Ir surface precovered with oxygen (0.5 L exposure at room temperature) leads to the formation of three-dimensional clusters that decorate atomic steps around the {111} and {001} faces of Ir (see Fig. 5).

When Cu is coadsorbed with O (background pressure during deposition about 5×10^{-9} Torr), beyond a shallow minimum an increase in the average work function is observed. When the coadsorption proceeds, the work function increases markedly above the value for clean Ir. The depth of the minima is considerably smaller than that in the case of Cu adsorption on the clean Ir tip at UHV, see Fig. 6.

A sequence of microscopic patterns which represent the result of heating a thick coadsorption layer of Cu and O, is shown in Fig. 7a–f. Figure 7a presents the FEM pattern of the initial surface of the Ir tip. On this surface a coadsorption layer of a thickness of some tens of monolayers was deposited at liquid nitrogen temperature. The result of heating this layer at a temperature of 430 K for 60 s is illustrated in Fig. 7b. It is seen that a part of the tip surface that is directly exposed to the source of the atomic beam is adsorbed. The portion of the tip "invisible" from the side of the source remains nonadsorbed. Having the tip heated to 650 K reveals coalescence of the adsorbate. As it is seen in Fig. 7c the grown crystallite shows a high degree of order. Clearly seen is a threefold symmetry typical of the (111) face of the cubic structure. A FEM pattern of the remaining part of the tip surface is similar in some details to that of oxygen adsorbed iridium (the {011} Ir faces). A further heating of the tip up to 720 K results in a decay of the crystallinity of the coadsorbate. The low temperature of coalescence and crystallization as well as the cubic structure produced indicate that the grown crystal could be formed by Cu_2O. Also a very low dissolving temperature of the crystal confirms it. As a result of the oxide dissolution the whole of the emitter surface was uniformly covered by an amorphous layer of a granular structure (Fig. 7d). It was observed that the size of grains increased with increasing the temperature of heating. The topography of the surface after heating to 1090 K is shown in Fig. 7e. The growth of the grains and a recovery of their crystallinity are noticeable. Since the background pressure during this experiment was not higher than 2×10^{-10} Torr and the equilibrium oxygen partial pressure for Cu_2O formation is about 10^{-8} Torr, the crystallites observed could be only Cu crystallites. Above
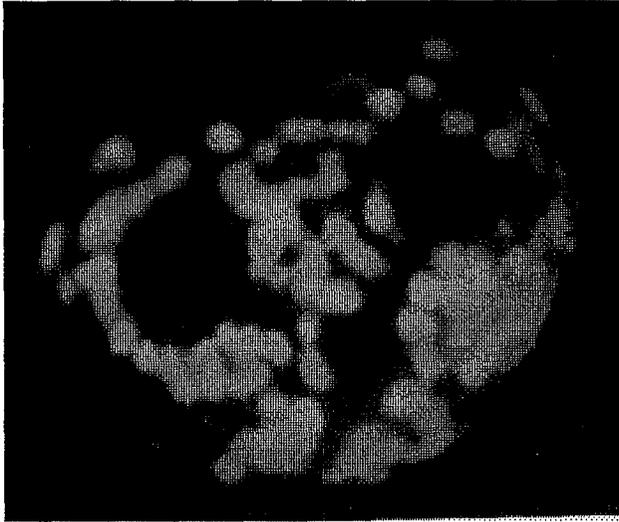
Fig. 5. FEM pattern of three-dimensional nuclei decorating edges of atomic steps around the faces {111} and {001} of Ir. The state after deposition of Cu onto Ir tip preadsorbed with oxygen at room temperature.
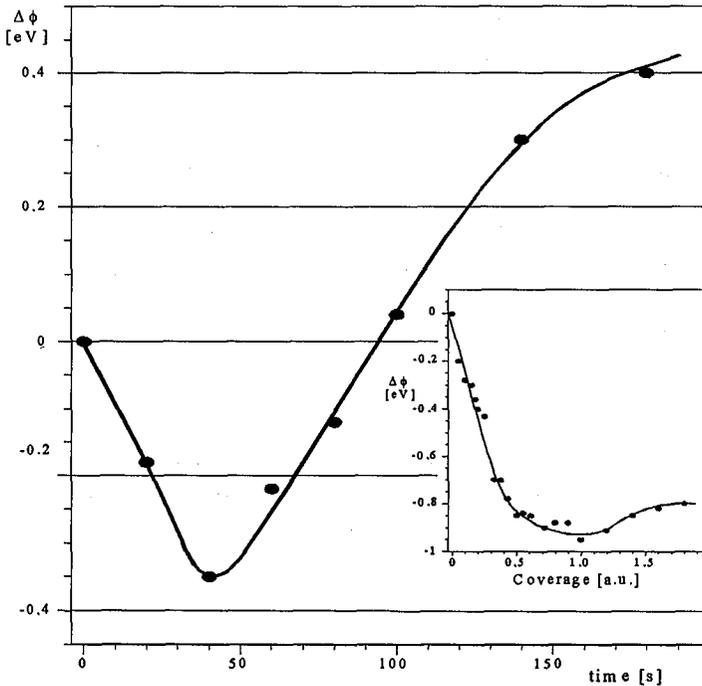

Fig. 6. Changes of the average work function caused by Cu adsorption on Ir tip precovered by oxygen. An inset at the lower right corner shows average work function changes caused by Cu adsorption on the clean Ir tip under UHV.
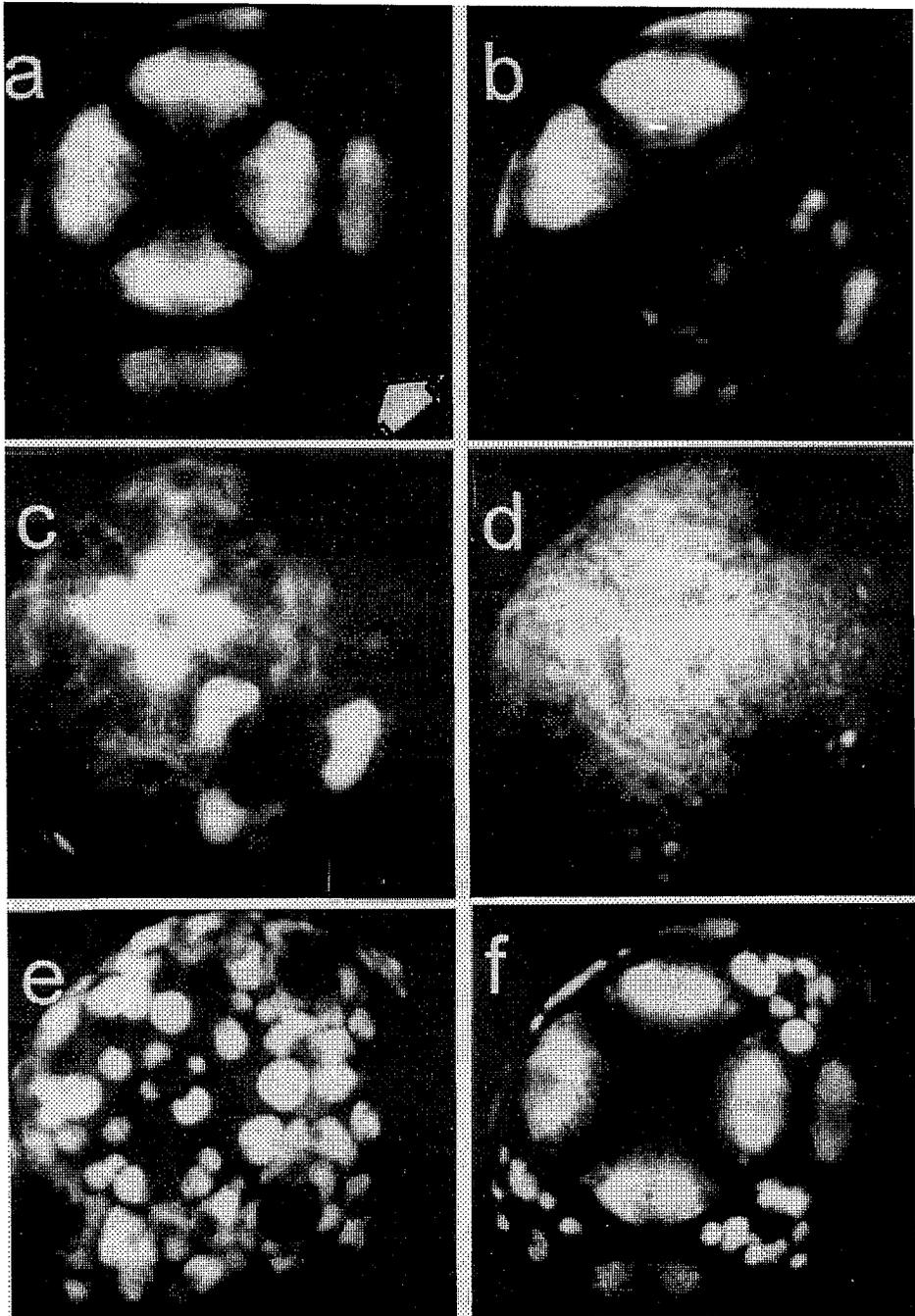
Fig. 7. FEM patterns illustrating selected evolution stages of the coadsorption layer of Cu and O during the course of raising the temperature of coadsorbate: (a) Clean substrate, the arrow indicates the direction of deposition. (b) Liquid nitrogen temperature deposited adlayer after heating it to 430 K. (c) After further successive heating to 650 K, (d) to 720 K, (e) to 1090 K (f) to 1160 K. See the text for details.
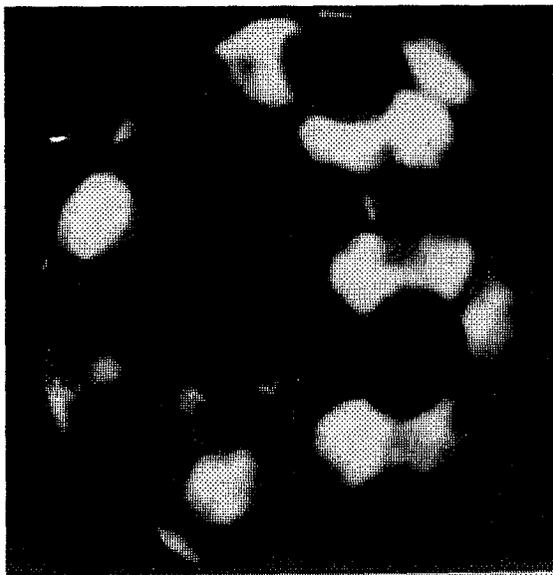
Fig. 8. Single crystallites of Cu formed on the {111} faces of Ir after Cu deposition by the Cu beam containing oxygen (background pressure less than 3×10^{-9} Torr) on the tip kept at temperature higher than 1090 K. The crystallites are epitaxially oriented toward the substrate with {111} Cu ∥ {111} Ir and ⟨011⟩ Cu ∥ ⟨011⟩ Ir.

1090 K the thermal decay of three-dimensional Cu crystallites begins on the {001} Ir faces and their terraces. After raising the tip temperature to 1160 K the copper crystallites remain only on the {111} Ir faces (Fig. 7e). A prolonged heating of the tip at the same temperature leads to disappearance of the three-dimensional Cu crystallites from the tip.

Deposition of Cu from the flux containing oxygen (background pressure during deposition less than 3×10^{-9} Torr) led to the formation of polycrystalline layers if the tip temperature was lower than 1090 K. For the temperatures higher than 1090 K, single crystallites of Cu with various degrees of perfection were formed exclusively on the {111} Ir faces (Fig. 8). They were epitaxially oriented toward the substrate with {111} Cu ∥ {111} Ir and ⟨011⟩ Cu ∥ ⟨011⟩ Ir. Heating such layers above 1100 K never resulted in their coalescence. Most probably it was due to oxide formation on {011} and {001} faces of Ir. Evidence for this is supplied by FEM patterns obtained during the course of thermal cleaning of the tip after Cu–O coadsorption experiments. Heating above 1700 K resulted very often in FEM patterns such as the one in Fig. 4d. This indicates the chemical interaction between the oxygen and some areas of the Ir tip surface at deposition temperatures.

4. Conclusions

1. In the case of a very small amount of Cu on the (001) Ir face, at temperatures higher than 600 K, cohesion forces between Cu atoms prevail over the adhesive interaction, which leads to three-dimensional nucleation on this crystal

face. The magnitude of the cohesion forces depends on the amount of Cu accumulation on the (001) Ir and it decreases with an increasing amount of Cu. When the Cu coverage on the (001) Ir is near an atomic monolayer, then the adhesive attraction prevails over the cohesion interaction and the three-dimensional nucleation vanishes.

2. The nucleation and growth of Cu crystals by deposition onto the clean Ir tip under UHV conditions proceed according to the Stranski–Krastanov growth mode. The grown Cu crystals are oriented with {111} Cu ∥ {111} Ir and ⟨011⟩ Cu ∥ ⟨011⟩ Ir. A large crystal of the curvature radius being equal to tens of nanometers epitaxially oriented to the substrate can be obtained as a result of coalescence by raising the temperature of the adlayer above 1100 K.

3. The presence of oxygen on the Ir surface is accompanied by an increase in cohesion interaction between atoms of the Cu deposited onto the tip at room temperature. The cohesion forces prevail over the adhesive forces, particularly on the edges of the atomic steps of the faces {001} and {111} of Ir. The superiority is maintained independently of the amount of Cu deposited. It is not clear whether the nuclei consist of pure Cu or they have an oxide nature.

4. Coadsorption of Cu and O on the Ir tip surface at liquid nitrogen temperature, when followed by gradually heating the adlayer, results in crystallization of the deposit in the temperature range from 430 K to about 700 K, whose range typically is not favorable for crystallization of Cu alone on the Ir tip. A complete decay of the crystals grown in such a way at temperatures higher than 720 K, indicates the formation of Cu_2O to occur with a high degree of crystallinity.

5. Cu and O coadsorption on the Ir surface at a temperature higher than 1090 K leads to selective accumulation of Cu on the {111} faces and to epitaxial crystal formation, oriented to the substrate in the same manner as the Cu crystals grown at UHV from Cu flux not containing oxygen. Oxygen incorporated into Cu flux interacts preferentially with {011} and {001} Ir faces, where it can produce oxide layers.

Acknowledgments

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