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STUDIES OF NEGATIVE FIELD ION MICROSCOPY WITH TETRACYANOETHYLENE

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Abstract - Negative ion images generated by tetracyanoethylene (TCNE) under inverted field conditions in a field ion microscope have been investigated in more detail. The experiments confirm previous findings /1/ and reveal further unique ionization phenomena such as the discontinuous development of ring structures in the ion image, the oscillation of rings in size and switching between different ion emitting surface structures. The observation of these phenomena critically depends on maintaining a tip temperature lower than the ambient gas temperature. The phenomena are attributed to the formation of an electrically conducting polymer layer of TCNE and to an elastic response of the layer surface to the field stress. Thus field enhancing and ion emitting protrusions are formed.

I - Introduction

Last year image formation by negative ions in field ion microscopy was reported /1/. In these experiments organic image gases of high electron affinity, such as tetracyanoethylene (TCNE) and dichloro-dicyano-benzoquinone, were applied. Pure ion images without contributions from field electrons could be obtained. At emitter cathode potentials slightly above the onset of field emission, the electron emission but not the anion emission current was found to decrease with time in the presence of the organic image gas. This effect was attributed to the field induced formation of an electrically conducting polymer layer on the cathode surface by the image gas. Ion images with unusual ring structures were observed with TCNE and tip cathode temperatures slightly lower than the ambient gas temperature. These phenomena were also attributed to the effect of an electrically conducting organic deposit built up by condensation and field induced polymerization of the image gas molecules on the tip surface.

We have studied the formation of negative ion images by TCNE in more detail. To that purpose the dependence of field ion images on applied tip potential, time and tip temperatures were examined. The experiment revealed further unusual and unique ionization phenomena. We assume that an elastic behaviour of the charged polymer layer under field stress gives rise to the observed phenomena.
II - EXPERIMENTAL

The experiments were performed with a gas pressure of TCNE in the field ion microscope of about $2 \times 10^{-4}$ mbar measured by a Penning gauge. The gas inlet system and the microscope had to be heated to achieve a sufficient gas supply. The temperature of the microscope, i.e. the image gas temperature ($T_{\text{g}}$) in the experiments, was about 60 °C. The tip support, a copper block, was electrically heatable and connected to a cooling trap with a weak thermal connection to the remaining microscope. The temperature of the tip ($T_{\text{t}}$) was measured by an NTC resistor connected to the tip support.

W tips of larger radius of curvature (several 100 nm) were used as field cathodes. They were prepared from 0.127 mm W wires by electrochemical etching without further treatment. Electron microscopy of tips already used for imaging with TCNE revealed the deposition of an inhomogeneous thick polymer layer and an increase of the radius of the coated tip ranging from 1 to 2 µm. Accordingly, the diameter of surface structures giving rise to the formation of the bright rings in the ion image can be estimated to several hundred nm.

A sensitive video recording system was employed to allow the registration and facilitate the analysis of fast dynamic phenomena such as switching between different image structures. The long exposure time of several seconds required for taking photographs of the ion images did not allow to resolve these phenomena.

III - RESULTS AND DISCUSSION

The present experiments confirmed the previous finding /1/ that the appearance of the ring structures in the TCNE ion image depends on maintaining an emitter tip temperature $T_{\text{t}}$ lower than the ambient gas temperature $T_{\text{g}}$, and on the formation of a thick polymer layer by condensation and field polymerization of TCNE on the tip surface. The formation of a thick organic layer has been repeatedly established by electron- and in some cases also by optical microscopy and is again the effect of keeping the tip temperature lower than the gas temperature under field ionization conditions.

The TCNE field ion images are generated by the anion emission from the surface of the electrically conducting polymer layer. Since the polymer layer steadily grows under imaging conditions, the field strength on the surface of the layer slowly decreases and, accordingly, slightly changes the ion image on a time scale of minutes. The polymer layer also grows at field strengths somewhat lower than those required for an ion image. Thus the layer also grows in surface regions displayed by dark areas on the screen.

In Fig. 1 typical changes of the ion image with "increasing" tip potential are shown. (In the following the negative sign of the applied potential is omitted.) The tip was already coated by a polymer layer at the beginning of the experiments. The series starts with a tip potential slightly higher than the onset of negative ion emission. The potential of the last image (Fig. 1 m) is close to the onset of electron emission. The (coated) tip radius could not be determined but is estimated to be about 1 µm.
Fig. 1 (see caption on page 260).
Fig. 1 - Negative field ion micrographs obtained with TCNE at constant temperatures (T₀ = 52 °C and T₀ = 23 °C) and increasing tip potential. The tip potentials were 1.3 kV (a), -2.0 kV (b), -2.5 kV (c), -2.8 kV (d), -2.9 kV (e), -3 kV (f), -3.1 kV (g), -3.2 kV (h), -3.3 kV (i), -3.4 kV (k), -3.6 kV (l) and -3.7 kV (m).

Fig. 2 - Negative field ion micrographs obtained with TCNE at different times: 0' (a), 12' (b), 16.5' (c) and 24' (d). From (a) to (d) the tip temperature increased from T₀ = 30 °C to 62 °C. Gas temperature T₀ = 62 °C and tip potential = -2.4 kV.

Fig. 3 - Negative field ion micrograph obtained with TCNE showing the concerted switching of rings between two states.
The phenomena observed in the experiments of Fig. 1 are as follows:

1. Rings are formed from the bright spots. There is no continuous change in the emission pattern but always a switching from one to another emission pattern shown in the series.

2. In 1b and 1c the ion emission oscillates back and forth between two overlapping rings. It is interesting to note that the increase of the potential from 1b to 1c changes the relative position of the two rings.

3. Under the conditions of 1d, oscillations of the ion emission between several concentric rings of different diameters were observed. This is invisible again in the photograph but indicated by a broadening of the ring. Such oscillations are typical precursor phenomena to the splitting of one to two rings as observed in 1e.

4. The sequence 1a to 1e was repeated and the emission pattern could be reproduced at the same voltages as applied before. The ion images were found to be reproducible after variations of the tip potential at lower field strengths applied to the tip.

5. The number of rings increases with increasing tip potential. Small displacements of rings during the increase of tip potential and ordering of rings, for example, in a line as shown in Fig. 3 of Ref. /1/ were frequently observed.

6. The potential of the last two images are close to the onset of irreversible changes of the surface structure of the layer by electron emission. At a tip potential of about -4.2 kV the layer was destroyed and removed by a strong electron emission current.

In Fig. 2 the effect of time regarding a continuous growth of the polymer layer combined with a slow increase of the tip temperature, i.e. the decrease of \( T_s - T_p \) is shown at constant applied tip potential. The temperature difference was about 32 °C in 2a and zero in 2d. Under these conditions the number of rings also increase from 2a to 2c during a growth of the polymer layer. However, the ring structures disappear as shown in 2d when a condensation of TCNE is no longer possible. Since ring structures always slowly disappear at \( T = T_p \), it is very probable that field desorption of part of the layer or of certain morphological structures which are not renewed by condensation and polymerization of image gas molecules accounts for the vanishing of the ring structure.

The negative ion images produced by field ionizations of TCNE on the surface of a polymer layer coating the emitter tip are very dissimilar to positive field ion images reported so far. The most striking phenomena observed in TCNE anion images are the appearance of ring structures and their discontinuous change with increasing field strength applied to the surface of the organic layer, and dynamic effects such as the switching of ion emission from one surface structure to another and between two surface structures back and forth. A further instructive example of the latter effect is the concerted switching of three rings between two states as shown in Fig. 3. These ion emission phenomena do not fit into the models of image formation in field ion microscopy discussed so far.
In the previous paper /1/ it has been proposed that the ring structures arise from imaging of tips of field enhancing whiskers growing on the cathode surface by field polymerization of TCNE. However, such a whisker model does not explain many features of the emission pattern such as the regular shape of rings, their ordering in lines and, in particular, the switching of ion emission between different surface structures. Provided the ion images reflect local variations of the field strength on the emitter surface caused by morphologic discontinuities, many dynamic effects are only consistent with the assumption of rapid and reversible changes of the morphological state of the polymer surface.

These considerations led to the assumption that a polymer layer is formed by field polymerization which under field stress behaves very elastic at the applied tip temperatures. Accordingly, a small field stress on the layer surface may generate single small field enhancing tips which switch to circular elevations of the surface similar to a volcano at higher field strength. Subsequently, other field enhancing protrusions are formed with increasing field stress as observed in Fig. 1. The oscillations between two or more ion emitting structures may be due to small differences in free energy between several "stable" structures. The ordering of rings can be attributed to the presence of a polymer layer of varying thickness on the surface of which the field stress causes the formation of ion emitting protrusions.

The assumption of an elastic response of the polymer layer surface to the field stress solves many problems of interpretation of the ion images. However, a detailed discussion of the emission phenomena on the basis of this assumption is beyond the scope of this paper.

REFERENCE