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EVIDENCE FOR IMAGING CONDUCTING POLYMER FOAMS IN NFIM WITH TETRACYANOETHYLENE AND DICHLORO-DICYANO-BENZOQUINONE

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Abstract - Unusual ion images of polymer layers formed by field polymerization of image gas molecules have been reported for tetracyanoethylene (TCNE) under conditions of negative field ion microscopy (NFIM). In these experiments the tip temperature was slightly lower than the ambient gas temperature. The present study shows that negative field ion images and dynamic phenomena obtained with 2,3-dichloro-5,6-dicyano-p-benzoquinone under similar experimental conditions closely resemble those observed with TCNE. Furthermore it is shown that the ion images of both image gases and the observed dynamic phenomena arise from an elastic foam structure of the polymer layer. The rings and ring structures are attributed to the ion emission from bubbles extending out of the surface with electrically conducting surface layers.

I - INTRODUCTION

Pure negative ion images have been obtained in field ion microscopy (FIM) with organic image gases of high electron affinity /1,2/. In previous investigations of negative field ion microscopy (NFIM) tetracyanoethylene has been used almost exclusively. Unusual ion images and dynamic phenomena were observed for conditions of a continuous condensation of TCNE on the cathode tip i.e. for tip temperatures slightly lower than the ambient gas temperature. In addition it was found that a conductive polymer layer with elastic properties under field stress is formed by field polymerization of image gas molecules. Thus the negative field ion micrographs are images of the surface structure of this polymer layer.

This paper reports results of NFIM-experiments with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, see Fig. 1). In these experiments too, the tip temperature was lower than the ambient gas temperature to maintain a continuous condensation of image gas molecules on the tip surface. The ion images and dynamic phenomena obtained with DDQ closely resemble those observed with TCNE, thus providing evidence for the formation of a polymer layer with similar properties and a similar surface structure.

Fig. 1: "DDQ" (electron-affinity = 3.3 eV /3/)

The most striking phenomena in the ion images are rings and structures composed of rings. These phenomena are independent of the image gas applied. In previous interpretations /1,2/ we have attributed this image pattern to the growth of field-enhancing whiskers and to an elastic response of the polymer layer to the field stress thereby forming field-enhancing circular protrusions. However, careful
inspection of various ionization phenomena such as the clustering of rings revealed that neither of these interpretations can be correct. In this paper we report evidence for imaging of an electrically conducting polymer foam in NFIM with both image gases.

II - EXPERIMENTAL

The experimental set-up of the field ion microscope was the same as in the previous experiments /1,2/. Tungsten tips were used as field cathodes. The experimental conditions for NFIM with DDQ were as follows: gas pressure about $10^{-4}$ hPa (measured by a Penning ionization gauge), gas temperature ($T_g$) between 35 and 50 °C, and tip temperature ($T_t$) 10 to 15 °C less.

The ion images were recorded on a video tape in order to facilitate the analysis of dynamic phenomena. The figures show photographs of ion images taken from a monitor screen. The estimated diameter of the rings in the ion images is between several 100 nm and more than 1 μm.

The scanning electron micrograph of a W-tip covered with a polymer layer grown by field polymerization of TCNE is shown in Fig. 2. The morphology of the layer is different from that in the ion microscope because no protrusions with circular symmetry are found in Fig. 2. Accordingly the structure of the layer is changed by the transfer of the tip from the ion microscope under "vacuum" to atmospheric pressure conditions outside.

III - RESULTS AND DISCUSSION

Typical ring structures obtained with DDQ, and the increase in the number of rings with "increasing" voltage applied to the tip is shown in Fig. 3 by a sequence of ion micrographs. (In the following the negative sign of the tip potential is omitted). The elastic behaviour of the polymer layer coating the tip under field stress is indicated by displacement of single rings or groups of rings with increasing tip voltage and by oscillation phenomena. Examples of this are the switching of ion emission between two overlapping rings, and of concentric rings in size leading to broadened rings in Fig. 3. The ion images can be reproduced by cyclic variations of the tip potential within certain limits. These and other observations are not different from those already reported for TCNE /2/.

The crucial question is that of the origin of the bright rings in the ion images of DDQ and TCNE. Two interpretations of the ring structures have been given: in our first paper they were tentatively attributed to the ion emission from the tip of field-enhancing whiskers but without discussing the problem of the particular surface structure needed for this type of ion image. In the second paper /2/ ion emission from circular protrusions, similar to a volcano, formed by the field stress on an elastic polymer layer were assumed to generate the ring structures. However, renewed careful inspection of typical image phenomena led us to the conclusion that neither of these interpretations can be correct. For example, as shown in Fig. 3, clusters of rings are typically formed with increasing field strength in which the appearing new rings increase the size of the clusters and raise the density of rings in the clusters, while the diameter of the rings remains constant. In addition the sequence of ion images observed with increasing tip potential is reversible and can be repeated. Neither ion emission from whiskers which interact by columbia repulsion nor field induced circular protrusions of an elastic polymer layer can explain these and other basic phenomena of negative ion imaging.
Fig. 2:
Scanning electron micrograph of a W-tip covered with a polymer layer grown by field polymerization of TCNE. Scale: 1 cm = 2 μm.

Fig. 3:
NFIM-images obtained with DDQ at increasing potential from -2 kV (a) to -3 kV (f). Tip temperature (T₀) 26 °C, gas temperature (Tₚ) 37 °C, gas pressure 10⁻⁴ hPa. The ion images were taken from a monitor screen.
Fig. 4: NFIM-images obtained with DDQ showing the development of rings from points with slightly increasing voltage from a to f. The ion images are enlarged "freeze-frame" pictures taken from the monitor screen.

Fig. 5: NFIM-image (W/DDQ) showing the attachment and deformation of the rings.

$U = -3.1 \text{ kV}, \; T_e = 26 \; ^\circ \text{C}, \; T_g = 37 \; ^\circ \text{C}$

$P \sim 10^{-4} \text{ hPa}$
We believe that ion emission from an electrically conducting polymer foam is the origin of the unusual image pattern. The foam is assumed to have elastic properties at the elevated operation temperatures of the microscope and to consist of agglomerates of bubbles with electrically conducting membranes formed by field polymerization of image gas molecules. It is very probable that the gas inclusions consist of image gas molecules, and dicyane and chlorine released during field induced radical polymerization of the image gases. Unfortunately, an independent direct proof of the polymer layer's foam structure is difficult because the morphological structure of the foam layer is changed by removal of the tip from the ion microscope. Furthermore the layer was found to field evaporate in the positive mode of FIM. This is indicated by a continuous decrease of the tip potential needed for ion formation in FIM. Accordingly ring structures are not observed in the positive ion mode of FIM. In the following indirect evidence is given for a foam structure of the polymer layer. Although details of the structure are not known, basic image phenomena observed with DDQ and TCNE are consistent with this assumption.

The foam structure is mainly supported by the appearance of rings and clusters of rings in the ion image. These rings can be attributed to the ion emission from bubbles extending out of the surface. Since the image gas molecules condense on the surface they are predominantly supplied by diffusion to the ionization zone which is a circular area on the surface of the bubbles. This circular area increases in diameter with field strength up to a maximum value determined by the diameter of the bubbles. The "dark" area within the rings can be attributed to the lower image gas supply from the gas phase, and very probably also to a weak electron conductivity of the two-dimensional membranes. The weak conductivity causes a potential drop along the surface towards the tip of the bubbles under FI conditions.

In accordance with this interpretation bright spots are observed at the onset of ion emission (Fig. 4). Rings are formed from spots at slightly higher tip potential. Further increase of the potential leads to a continuous increase of the size of the rings up to a maximum of nearly constant diameter typically observed for all rings of an ion image. The constant diameter points to an equal shape of the bubbles. At still higher potentials the bubbles (or rings) attach to each other and deform in a similar way as observed in a different system for the transition for the so-called "kugelschaum" to the "polyederschaum" (Ref. 4). (see Fig. 5) This latter phenomena may be related to the effect of a shearing force on the bubbles. The origin of this shearing force is not clear yet.

The elastic property of a thick foam layer under field stress at elevated temperature becomes particularly obvious from the observations of correlated and uncorrelated displacements of rings and ring structures relative to each other in the ion images. Such displacements typically take place in a discontinuous manner and can be explained by the switching of a small part of the surface between two or more metastable positions. Since several of these dynamic phenomena frequently occur in a single ion image at the same time they can hardly be attributed to any other structure of a layer than to that of an elastic polymer foam.

The imaging field strength ($E$) near the onset of ion emission is probably near 0.1 V/Å. Accordingly the field stress is about 50 bar and grows with increasing field strength ($\alpha E^2$) by a factor of $\approx 3$ up to the onset of an irreversible destruction of the polymer layer. The major effect of the field stress on the charged bubbles is a change of the morphological structure of the foam surface in a way that more bubbles are exposed to high electric fields and thus appear in the ion image. Various dynamic phenomena observed during the increase of tip voltage can be attributed to this effect of the field.
IV - Conclusions

It was found that both image gases DDQ and TCNE give rise to the same phenomena in NFIM. These are the formation of a polymer layer by field polymerization, the appearance of rings and ring structures in the ion image of this layer and a variety of dynamic phenomena indicating fast variations of the morphology of the layer under field stress. Furthermore, evidence has been provided for a foam structure of the polymer layer and for imaging of agglomerates of bubbles with electrically conducting surface layers.

Although some basic features of NFIM have been explained, a detailed interpretation of the observed image phenomena is still not possible. The difficulties in interpretation are mainly due to the lack of an NFIM-independent knowledge of the surface and bulk structures of the polymer foam. In addition, the mechanism of polymerization and growth of the layer as well as its electronic structure is not clear yet.

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