ON THE SURFACE MORPHOLOGY UNDERLYING NFIM IMAGES OBTAINED WITH TETRACYANOETHYLENE

R. Schmitz, F. Röllgen

COLLOQUE DE PHYSIQUE
Colloque C8, supplément au n° 11, Tome 50, novembre 1989

ON THE SURFACE MORPHOLOGY UNDERLYING NFIM IMAGES OBTAINED WITH TETRACYANOETHYLENE

R. SCHMITZ and F.W. RÖLLGEN

Institute of Physical Chemistry, University of Bonn, Wegelerstrasse 12, D-5300 Bonn 1, F.R.G.

Abstract - The ring structures and dynamic phenomena observed in field ion microscopy with negative ions (NFIM) of tetracyanoethylene (TCNE) are interpreted as ion images of a surface layer grown by field-induced polymerization of the image gas molecules. The ring structures are attributed to the formation of mobile surface elevations by the field stress on the polymer layer. These small surface elevations combined with larger surface deformations, generated by the field stress and resulting from elastic properties of the bulk of the layer, explain many features of NFIM such as the clustering of rings and compression of ring structures.

I - INTRODUCTION

Unusual ion images with ring structures and dynamic phenomena were reported for field ion microscopy with negative ions (NFIM) of tetracyanoethylene (TCNE) and dichloro-dicyano benzoquinone [1-3]. The negative ion micrographs without electron emission were obtained for tip temperatures slightly lower than the ambient gas temperature [1]. The images were attributed to the imaging of a thick electrically conducting polymer layer formed by field polymerization of image gas molecules. The experiments also revealed elastic properties of the polymer layer under field stress.

The crucial question still left is that of the origin of the ring structures. Two years ago an elastic response of the surface of the polymer layer to the field stress was considered and circular elevations, which enhance the electric field, were thought to be formed by the field stress [2]. Since these elevatons were assumed to be locally fixed, this model could not explain, for example, the clustering of rings which is observed at higher field strengths. Accordingly, a different model was introduced last year relating the ring structures and the clusters of rings to the ion image of a foam structure of the polymer layer [3]. However, other features of negative ion images were found to be more difficult to explain. In particular the direction of the shearing force resulting in a compression of rings in a cluster at higher field strengths is opposite to that created by the field stress on agglomerates of bubbles extending out of the surface of a polymer layer.

This ring compression effect and other phenomena discussed below lead us to the conclusion that the field-enhancing surface protrusions forming the ring structures are not locally fixed but mobile on a smooth surface. Accordingly, the surface protrusions forming the ring structures and created by the field stress must be due to small elastic deformations of the polymer layer surface.

The present model of the morphological surface structure underlying the negative field ion images is closely related to the first model [2] mentioned above. In that previous model both a bulk and surface elasticity of the polymer layer were already considered but not the surface mobility of small elevations.

In the following the basic model assumptions are briefly described and some features of negative ion images obtained with TCNE are interpreted. The experimental set-up and conditions applied to obtain the displayed NFIM images with TCNE were the same as reported in Ref. [2].

II - FIELD STRESS EFFECTS ON THE SURFACE MORPHOLOGY

The chemical structure of the polymer layer is not known yet, but it is probable that field polymerization of TCNE leads to an amorphous and loose overlayer structure with a high surface and bulk elasticity. The surface elasticity gives rise to the formation of small field enhancing elevations under appropriate conditions of a high field stress on the surface. The bulk elasticity and field stress are responsible for larger deformations of the surface. The increase in surface curvature leads to field enhancement in larger areas of the surface. Both field stress effects and a mobility of small field enhancing elevations on smooth parts of the polymer layer surface are important for the interpretation of the negative ion images. The field stress corresponding to a field strength of 0.1 V/Å is about 50 bar.

Negative ion images obtained with TCNE as function of the applied tip potential between the onset of ion emission and the onset of electron emission resulting in a destruction of the layer have been reported [2]. The emission pattern, which consists of spots, rings, clusters of rings etc., can be attributed to the ion emission from field enhancing surface protrusions generated by the field stress on the polymer layer surface. The observed switching of the ion emission from one to another emission pattern or the oscillation of the ion emisson back and forth between different patterns such as concentric rings of different diameters or overlapping rings [2] show that the surface protrusions once formed are not stable but can rearrange. Such quick and reversible changes of the surface morphology are in accordance with the assumption of small surface elevations formed by the field stress.

Evidence for mobility of the ion-emitting surface elevations is provided by the continuous movement of rings relative to each other which is frequently observed by varying the tip potential [1,2]. The driving force for this movement is a field strength gradient along the surface, i.e. the surface protrusions move to areas of higher field strength. The field strength distribution in a surface area is changed by an increase of the surface curvature due to the applicaton of a higher field stress and the elastic response of the layer. Thus the clustering of rings with increasing field strength can be attributed to the movement of the corresponding ion emitting circular elevations from the shank to the apex of a curved surface. Furthermore the appearance of a shearing force resulting in a compression of ring clusters at high negative tip potential (Fig. 1) can be explained by the effect of a strong field stress gradient in the apex area of a large surface protrusion.

The phenomenon of clustering of rings in rows (Fig. 2) indicates ellipsoidal-like deformations of the surface. The occurance of several clusters of rings in the ion image and the relative movement of these clusters upon field strength variation (Fig. 3) point to a more corrugated surface of the polymer layer. Such a corrugated surface is also seen in scanning electron micrographs of tips coated by the polymer layer of TCNE which were exposed to atmospheric conditions before inserting them into the electron microscope (see Fig.2 of Ref. [3])

The observation that the ion images remain basically unchanged during a continuous growth of the layer by field polymerization, provided the a b

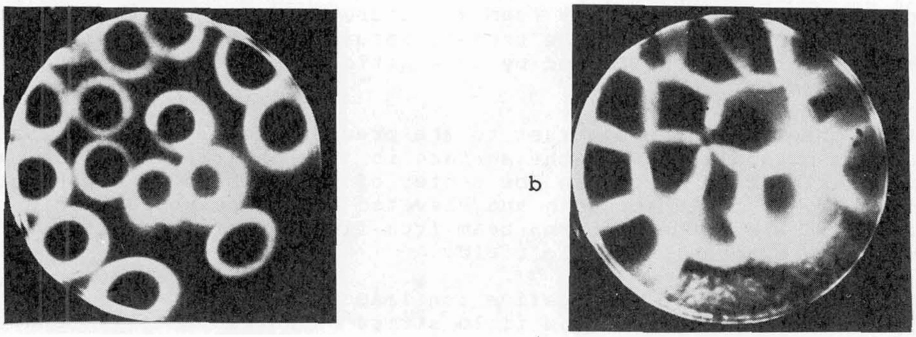

Fig. 1: NFIM-images showing the clustering of rings (a) and the appearance of a shearing force, which results in a compression of ring clusters (b).

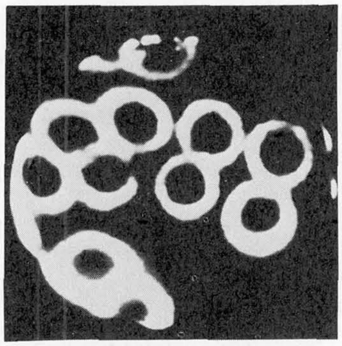

Fig. 2: NFIM-image showing the clustering of rings in rows.

a b

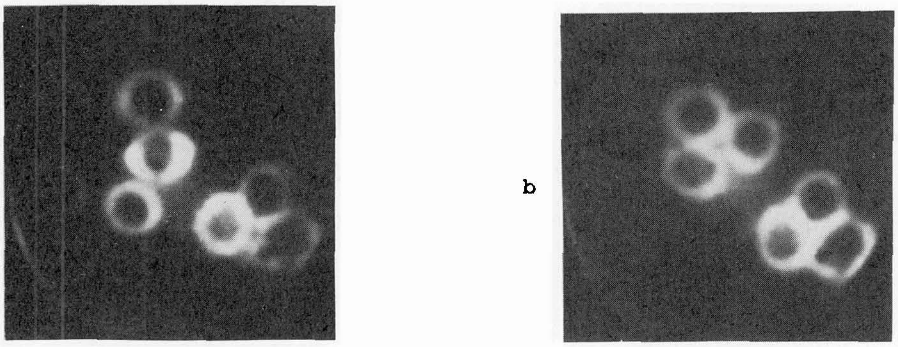

Fig. 3: NFIM-images showing two ring clusters and the effect of a slight increase of the applied negative tip potential from (a) to (b).

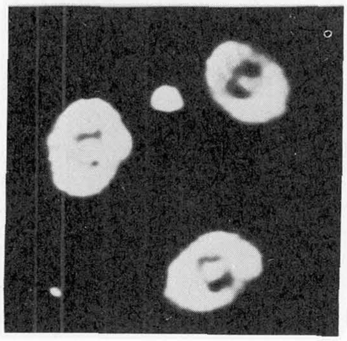

Fig. 4: NFIM-image showing ion and electron emission from a spot in the center of rings. The bright spot at the right side is due to the electron emission from the center of the upper ring deflected by an external magnetic field. Tip temperature: 52 °C, and gas temperature: 59 °C.

negative tip potential is slightly raised to correct for a decrease of the surface field strength, is in strong contrast to the previous model of image formation based on a foam structure of the polymer layer. However, it is in support of the present assumption of ion emission from small surface protrusions formed by an elastic response of the layer to the field stress.

A further observation in contrast to the previous model of ion emission from bubbles extending out of the surface is the phenomenon of ion and electron emission from a spot in the center of rings which is occasionally found at higher field strength and elevated tip temperature. This is shown in Fig.4 where the electron beam from field electron emission is deflected by an external magnetic field.

A detailed discussion of negative ion images obtained with TCNE is difficult because the effect of a field stress on an elastically behaving polymer layer is not known from other experiments. However, we believe that the present assumption about the morphological surface structure underlying the negative ion images provides a key for a correct interpretation of the various phenomena observed in NFIM with TCNE.

Acknowledgement

Financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

1. R.Schmitz, L.Bütfering and F.W.Röllgen,
J. de Physique 47 (1986) C7-53.

2. R.Schmitz, F.Okuyama and F.W.Röllgen,
J. de Physique 48 (1987) C6-257.

3. R. Schmitz and F.W. Röllgen
J. de Physique 49 (1988) C6-243.