Charge flow during metal-insulator contact

C. Schönenberger*
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
(Received 26 September 1991)

The electrification of polymethyl methacrylate films is studied by scanning force microscopy. Charged areas generated by contact electrification are always found to be larger than those generated by corona discharge, and are surprisingly much larger than the area of contact. After each single contact made with the metal tip on the insulator charge was transferred, the sign of which was arbitrary. It is argued that charge already flows and spreads into the insulator at the time of metal-insulator contact.

I. INTRODUCTION

The electrification of insulators by contact or friction is a long-known phenomenon of technological importance. Despite having been the subject of much research little is known about the charge transfer itself. In this paper electrification experiments on polymethyl methacrylate (PMMA) films using scanning force microscopy (SFM) are described.

SFM is a powerful instrument for mapping the surface topography of virtually any solid with a spatial resolution ranging down to a single atom.[1] The idea is to measure and control the core repulsive force between the foremost atom of the probing tip and the surface to be imaged. When the contact between the tip and the sample is broken, the electromagnetic interaction force is accessible. Due to its long-range nature this interaction is generally not confined to the foremost apex atom of the tip, hence an atomic spatial resolution cannot be achieved. Instead, the resolution is given by the macroscopic radius of the probing tip, typically 10–100 nm. The magnetic dipolar interaction between a ferromagnetic tip and the magnetic stray field of a ferromagnetic sample is now widely used to investigate domain structures and, in particular, to study intentionally written bit patterns.[2] Similarly, the electrostatic Coulomb force can be utilized to image the surface potential of devices,[3] ferroelectric domain walls,[4] and dopant distributions in semiconductors.[5] Moreover, Stern *et al.*[6] and Terris *et al.*[7] have studied the deposition of local charge onto insulators by corona discharge and contact electrification, respectively. The recent observation of discontinuous charge decay by SFM has demonstrated that single-charge-carrier sensitivity is possible.[8]

A major puzzle in the electrification of insulators is the origin of irreproducibility: even the sign of the charge exchanged in experiments on a single sample varies from measurement to measurement.[9] Moreover, macroscopic contacting experiments show —sometimes surprisingly— that the total amount of charge transferred can be steadily increased by repeatedly touching the insulator on the same spot with the same metal sphere.[10,11] If, in these experiments, contact was indeed established on exactly the same spot, thermal equilibrium cannot have been achieved in a single contacting event. Due to asperities on the metal sphere and the insulator, a multiple contact may have been established. Repeated contact progressively flattens the asperities such that the true area of contact increases. Here, the SFM offers the unique possibility of making contact on a very small area ranging down to a few atoms and of imaging the areas charged with high spatial resolution thereafter. The problem of making multiple contacts can thus be circumvented.

An important parameter for theoretical modeling is the surface charge density.[12] Since macroscopic experiments do not allow the true area of contact nor the area charged to be measured, it is difficult to derive this quantity experimentally. Typical reported charge densities are 10^{-4} C/m^2 corresponding to about 1 elementary charge in 10^4 surface atoms. Contact electrification is clearly a small effect on an absolute scale and is expected to be rather sensitive to surface contamination. Unfortunately, a great deal of experimental work, including that described here, was performed in air under ambient conditions. However, no substantial difference is found in experiments performed in a moderate vacuum, indicating that electrical breakdown in air cannot be the cause of the problems described.[9] In the excellent review article by Lowell and Rose-Innes,[11] several fundamental questions are raised. One of these is the question of whether charge is transferred exclusively to surface states within the area of metal-insulator contact or whether a subsequent charge transfer to the bulk of the insulator plays a role as well. This question will be addressed below.

II. EXPERIMENT AND DISCUSSION

The instrument used in this investigation has been described elsewhere.[12] Degenerately doped GaAs wafers serving as conducting substrates were spin coated with PMMA film like those used in electron-beam lithography. The film thickness was measured by ellipsometry. Etched tungsten tips were used as SFM probes.

Figure 1(a) is a schematic of the tip apex positioned at distance d above an insulating film of thickness h. A voltage V applied to the tungsten tip results in the Coulomb force $F=(V+\phi)^2G$, where G contains dielectric and geometrical parameters such as the tip radius R and the tip-sample distance d. The term ϕ is the contact

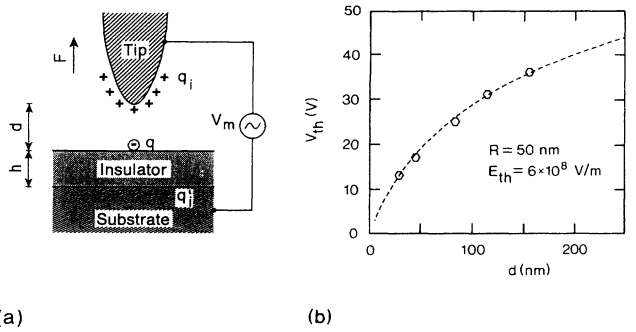


FIG. 1. (a) Schematic explanation of the detection of the excess charge q on an insulating film via the force F_1 related to the image charge q_i, and (b) the threshold voltage V_{th} for corona discharge as a function of the tip-sample distance d.

potential between tip and sample. We apply an ac voltage $V=\sqrt{2}V_m\sin(\omega t)$ and measure the rms amplitudes of the forces F_1 and F_2 oscillating at frequencies ω and 2ω, respectively. The parameter G and hence the tip-sample distance is controlled via F_2, whereas ϕ is extracted from F_1 (details can be found in Refs. 7 and 8). The gray scale of the following images corresponds with measured F_1 values. A charge carrier q lying on the surface of the insulator induces image charges q_i and q_i' in the tip and the conducting substrate, respectively [Fig. 1(a)]. Since neutrality requires $q_i+q_i'=-q$, the magnitude of q_i/q is always less than unity, and it increases when the ratio of the tip-sample distance d to the film thickness h is decreased. The value of F_1 is given approximately by $F_1=q_iE_a$, where E_a is the rms electric field at the tip apex due to the applied ac voltage.

The corona discharge (CD) is initiated by the temporarily interrupting the controller loop and applying a dc voltage pulse (typically 10 V) of 10 ms duration. After this, the charge deposited is monitored by a change in the force signal F_1. Figure 1(b) displays the threshold voltage V_{th} as a function of the tip-sample distance d for a tip having an effective radius of $R=50$ nm. The dashed curve is calculated assuming a constant threshold field of 6×10^8 V/m.[8]

The possibility of depositing charge on an insulator locally and following its temporal and spatial evolution by imaging allows the migration of excess charge in insulators to be studied. Figure 2 shows the smallest amount of negative charge we were able to transfer into a film of thickness $h=300$ nm. The picture size is 1 μm^2. Figure 2(b) shows the measurement at 100 s and Fig. 2(c) at 2000 s after the CD. The experimental parameters are $d=10$ nm, $R\leq30$ nm, and $E_a\geq0.5\times10^8$ V/m. The charge appears as a bright spot at the center of the images with an apparent diameter of ≈70 nm limited by the lateral resolution given by the tip radius R. The evolution of the charge signal was monitored over 5000 s and the peak signal with respect to the background is shown in Fig. 2(a). The bars to the right give the expected signals for one ($n=1$) and two ($n=2$) excess electrons, suggesting that the number of deposited charges was 2. The rather strong scatter in the data arises from the electrical inhomogeneity in these films and is not due to limited instrumental sensitivity. If the excess carriers were to move toward the substrate, F_1 would decrease and the imaged charge area would become broader. A decay is seen in Fig. 2(a), but no broadening is observable, indicating that the carriers remain at their initial positions. The continuous decay is presumably the result of the screening effect of residual charge carriers that are allowed to move toward the excess charge due to the finite surface and bulk conductance of the insulator.

In contact electrification (CE) the controller loop is temporarily interrupted as well and the sample is moved over a preselected distance towards the tip. The recorded static force versus displacement indicates contact as the force becomes repulsive. The repulsive load force was controlled between 10^{-7}–10^{-8} N. The tip was kept electrically isolated during this procedure.

The irreproducibility known from macroscopic CE experiments is also found in our SFM experiments. Three representative images of areas charged by CE are displayed in Figs. 3(a)–3(c). A bright (dark) spot with respect to the background corresponds to positive (negative) charge on the film. In similar experiments Terris *et al.*[7] sometimes found that two charge spots of opposite sign were generated simultaneously after a single contacting event. This phenomenon was termed bipolar charge transfer and can account for the irreproducibility since macroscopic experiments always measure the total amount of charge transferred. Hence, positively and negatively charged areas will partially cancel each other and a broad charge distribution of the net exchanged charge is to be expected. Despite intensive research we never

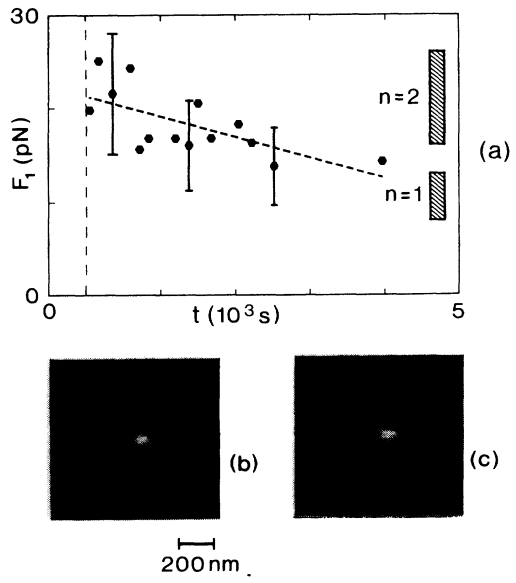


FIG. 2. (a) Imaged charge area on a PMMA film and its decay. The shaded bars indicate the expected signal (with its uncertainty bar) for n excess electrons. Parts (b) and (c) were imaged 100 and 2000 s, respectively, after charging.

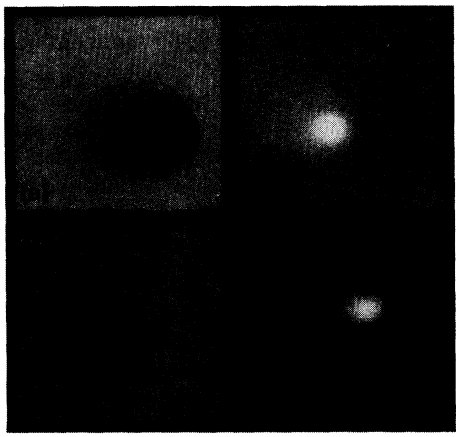


FIG. 3. (a)–(c) areas charged by contact electrification on a PMMA field of thickness 300 nm. The bright (dark) spot corresponds to positive (negative) charge on the insulator. In part (d) the positively charged area was created by contact electrification and the other two negatively charged areas by corona discharge. All images represent an area of $4\times4\ \mu m^2$.

found bipolar charge transfer in a single contacting experiment on our films. Since the same irreproducibility is found in our microscopic experiments, bipolar charge transfer cannot generally account for it. The measurement parameters for the images in Figs. 3(a)–3(c) are $V_m=5$V, tip-sample distance $d=30$ nm, tip radius $R=50$ nm, film thickness $h=300$ nm, and dielectric constant of the film $\epsilon=2.25$. The absolute force F_1 measured at the center of the charged areas is 200 pN on average. This allows the charge density σ to be estimated. The apex electric field is calculated to be $E_a=8\times10^7$ V/m and q_i/q is about 0.5.[8] The value of σ is estimated from $q/R^2\pi$ which yields 5×10^{-4} C/m^2. This is a bit larger than the 10^{-4} C/m^2 typically found in macroscopic experiments. About 1000 carriers are transferred. This amount is probably underestimated since charge carriers transferred deep into the bulk of the insulator give rise to a smaller force signal than assumed.

The most striking and most reproducible observation made is the large area apparently charged by CE. The diameter of the imaged spot is typically found to be 500 nm. In Fig. 3(d) the central bright spot was generated by CE and the other two dark ones by CD with the same tip. The much smaller apparent charge area produced by CD proves that the instrumental resolution power is not the limiting factor. CE is always found to charge an area larger than CD. Figure 2 has already demonstrated that very small areas can be charged by CD, whereas CE never charged areas smaller than 300 nm in diameter. Furthermore, the recorded temporal evolution of the charge signal reveals no difference for charged areas produced by the two methods. This indicates that equivalent trap states are occupied in both cases. Moreover, the possibility of the charge spreading during tip retraction due to an electric breakdown between the metal tip and an initially densely charged area on the insulator can be excluded as well. This scenario would be equivalent to a corona discharge which evidently charges much smaller areas. It thus appears that a metal in contact with a polymer induces some charge transport in the insulator allowing the charge to be spread over distances up to 1 μm. From the estimated amount of carriers transferred, the measured size of charged areas, and the typical trap state density of 10^{22}–10^{24} m^{-3} for polymers, we deduce that the depth to which charge is transferred is larger than 10 nm. However, there might be sufficient surface trap states such that all charge is on the surface after spreading. In this case a strong dependence of the charge decay rate as a function of surface conductance is expected. The ion concentration of the unavoidable absorbed water layer on the PMMA films was varied but no significant change in the decay time was found. This we take as an indication that charge is indeed transferred into bulk trap states.

The charge has to spread during the contacting process as can be seen from the following argument. For a spherical tip of radius R the contact area is a circular disk with radius r. From macroscopic elasticity theory the load force is $F=4E'r^3/3R$, where E' is an effective elastic constant.[13] Taking $F=10^{-8}$ N and $E'=4$ GPa results in $r\simeq4$ nm and a large pressure of 200 MPa exceeding the tensile strength of PMMA of $\simeq70$ MPa. The film is therefore most likely to be plastically deformed at the point of contact. Taking the tensile strength of PMMA as the maximum pressure, the radius of the contact disk is estimated to be $r\simeq7$ nm. Assume that the 1000 carriers were to be transferred into available surface states within the contact disk. This would correspond to an enormously large charge density of 1 C/m^2 and to unrealistic surface electric fields as large as 10 V/Å. Hence, it can be concluded that charge flow has to occur during the metal-insulator contact. It may be that the large pressure of 70 MPa is responsible for the conductivity. However, the pressure in the material decays with the characteristic length r, a length much shorter than the diameter of the charged areas. Pressure-induced conductivity can therefore not account for the observed transport effect.

III. CONCLUSION

The local electrification of PMMA films has been studied by scanning force microscopy. The films are charged both by corona discharge and contact electrification using SFM and the areas charged are imaged with the same instrument. CD is capable of charging very small areas and the time evolution indicates that the transferred carriers are immobile. Charged areas created by CE, on the other hand, are always found to be larger than those generated by CD, and —surprisingly—far exceed the contact area whose radius can be kept as small as 7 nm. The amount of charge exchanged shows the characteristically wide distribution similar to that known from macroscopic experiments. On our films we have been unable to confirm bipolar charge transfer found recently in similar experiments.[7] As discussed, the experimental results on CE provide clear evidence for charge flow during the metal-insulator contact. It is therefore not possible that charge is only exchanged into surface states during con-

tact and is allowed to spread by its own Coulomb repulsion after the conducting metal tip has been withdrawn. Furthermore, charge flow is probably not restricted exclusively to the surface, and bulk states may be relevant to the physics of charge transfer. We feel that the possibilities offered by SFM to charge insulators very locally and to image the charged areas with high resolution combined with classical electrometers will help elucidate many of the yet unsolved questions regarding insulator electrification. Further experiments should preferably be performed in good vacuum and on model systems that are easy to prepare, for example, on semiconductors.

ACKNOWLEDGMENTS

This work was done in collaboration with S. F. Alvarado and M. Lutz. The author would like to thank S. F. Alvarado for his continuous support and interest in this work, as well as H. Rohrer for motivation and stimulating support.

---

*Present address: Philips Research, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands.

[1]G. Binnig, C. F. Quate, and Ch. Gerber, Phys. Rev. Lett. **56**, (1986) 930.

[2]C. Schönenberger and S. F. Alvarado, Z. Phys. B **80**, (1990) 373; for a review see P. Grütter, H. J. Mamin, and D. Rugar in *Scanning Tunneling Microscopy,* edited by H.-J. Güntherodt and R. Wiesendanger (Springer, Verlag, in press).

[3]Y. Martin, D. W. Abraham, and H. K. Wickramasinghe, Appl. Phys. Lett. **52**, 1103 (1988).

[4]F. Saurenbach and B. D. Terris, Appl. Phys. Lett. **56**, 1703 (1990).

[5]D. W. Abraham, C. Williams, J. Slinkman, and H. K. Wickramasinghe, J. Vac. Sci. Technol. B **9**, 703 (1991).

[6]J. E. Stern, B. D. Terris, H. J. Mamin, and D. Rugar, Appl. Phys. Lett. **53**, 2717 (1988)

[7]B. D. Terris, J. E. Stern, D. Rugar, and H. J. Mamin, Phys. Rev. Lett. **63**, 2669 (1989).

[8]C. Schönenberger and S. F. Alvarado, Phys. Rev. Lett. **65**, 3162 (1990).

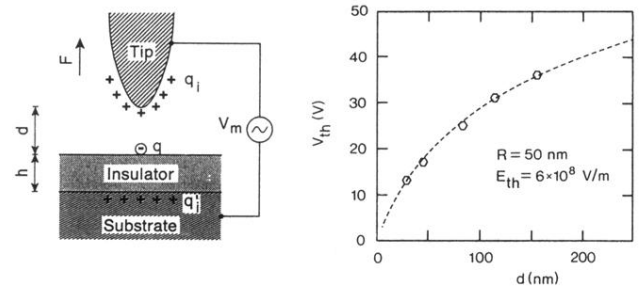
[9]J. Lowell and A. R. Akande, J. Phys. D **21**, 125 (1988).

[10]T. J. Fabish and C. B. Duke, J. Appl. Phys. **64**, 2218 (1988).

[11]J. Lowell and A. C. Rose-Innes, Adv. Phys. **20**, 947 (1980).

[12]C. Schönenberger and S. F. Alvarado, Rev. Sci. Instrum. **60**, 3131 (1989).

[13]L. D. Landau and E. M. Lifschitz, *Theory of Elasticity,* Course of Theoretical Physics (Pergamon, New York, 1959), Vol. 7, p. 30.



(a) (b)

FIG. 1. (a) Schematic explanation of the detection of the excess charge q on an insulating film via the force F_1 related to the image charge q_i, and (b) the threshold voltage V_{th} for corona discharge as a function of the tip-sample distance d.

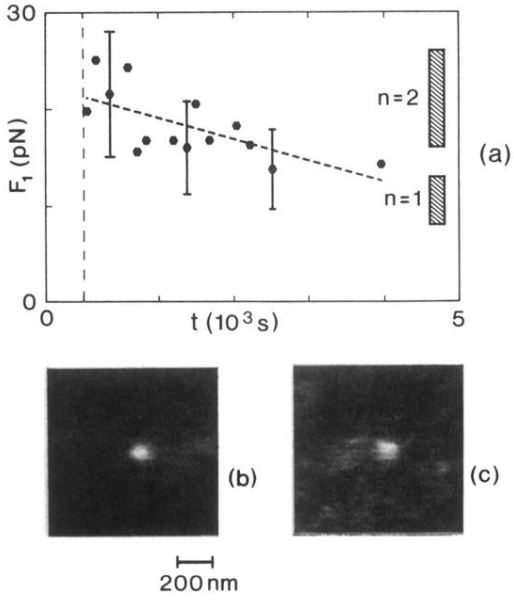


FIG. 2. (a) Imaged charge area on a PMMA film and its decay. The shaded bars indicate the expected signal (with its uncertainty bar) for n excess electrons. Parts (b) and (c) were imaged 100 and 2000 s, respectively, after charging.

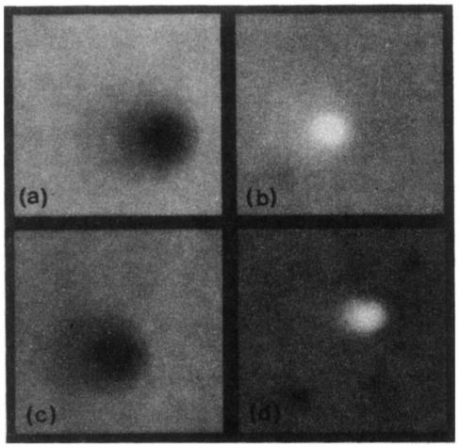


FIG. 3. (a)–(c) areas charged by contact electrification on a PMMA field of thickness 300 nm. The bright (dark) spot corresponds to positive (negative) charge on the insulator. In part (d) the positively charged area was created by contact electrification and the other two negatively charged areas by corona discharge. All images represent an area of $4\times4\ \mu m^2$.