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1989 J. Phys.: Condens. Matter 1 9823

(http://iopscience.iop.org/0953-8984/1/49/003)

J. Phys.: Condens. Matter **1** (1989) 9823–9831. Printed in the UK

A shear model for STM imaging of layered materials

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Received 17 July 1989, in final form 4 September 1989

Abstract. We have modified a precision indentation device to allow STM rastering of a tip across a surface, while simultaneously monitoring mechanical contact. Images obtained from this apparatus on a HOPG sample exhibit atomic scale resolution with contact areas much larger than a single atom. We provide a model for this process as shear between atomic planes. The model explains a variety of curious, and otherwise unrelated phenomena occurring during STM imaging of these materials.

1. Introduction

There has recently been considerable interest in sub-micrometre size contacts, especially between conductors. The restrictions to electron transport due to small contact areas may lead to ballistic motion and quantum effects, which are highly relevant to those who would further miniaturise semiconductor devices. For example, the resistance between 2D electron gas reservoirs of GaAs and AlGaAs has been shown to be oscillatory as the contact area is changed [1]. Furthermore, such extremely localised contact provides a means of investigating some of the novel mechanics of the near-atomic scale, such as ideal lattice strengths [2, 3].

Aside from the interest on behalf of device technology, the 'nanocontact' field has significance for scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). In this paper we describe the use of a new point probe method to study the characteristics of contact in STM. Even in the juvenile phase of STM, Smith and co-workers [4] demonstrated how imaging of highly oriented pyrolytic graphite (HOPG) could be achieved with tip and surface in contact. More recently, Gimzewski and Möller [5] measured the tip–sample resistance during the transition from STM to point contact in UHV. They observed a sequence from vacuum tunnelling, through a spontaneous jump into contact [6], to a contact resistance close to the expected quantised value [5, 7]. In this paper we suggest that the standard picture, of tunnelling from a single atom across an air or liquid gap, is misleading in STM experiments performed on certain materials under non-UHV conditions. Contact can be demonstrated and the imaging mechanism cannot clearly be established to involve fluctuations in tunnelling current, rather than another form of conductance. We show that imaging is likely to involve conductance over an area larger than a single atom, and consequently that the 'contrast' of the images is due to the periodic misalignment of atomic planes during shearing.

2. An alternative to single-atom tunnelling

The high probability of surface contamination in air, under water or in aqueous electrolytic solution makes atomic resolution STM under these conditions remarkable. Generally a layered material such as HOPG or a transition metal di-chalcogenide is involved [8], or there are easy shear planes parallel to the surface. A careful inspection of published images of this type reveals some common features:

(i) the images are often regular in periodicity over large areas [9] (although the repeated pattern may be complex) and there is a notable absence of point defects;
(ii) any non-periodic features that are resolved appear blurred or extend over several lattice spacings, and the lattice itself may be seen superimposed through the feature [10];
(iii) corrugation amplitudes can be excessively large and the barrier height, as measured for example by $\partial \ln I/\partial z$, is generally much lower than the work function.

These observations are in fact all interrelated and can be explained if it is postulated that the tip and sample are intimately in contact—contact involving at least a few atoms rather than just the overlapping electron clouds of two. Thus the first four anomalies are the inevitable consequence of averaging the imaging current over several atoms, while the giant corrugations and low barrier heights result from the magnification of tip motion due to elastic contact over a large area [11, 12]. This issue is of considerable importance in STM imaging in a non-UHV environment, as the implication is that the probe is not real-space on the atomic scale, but only over some larger area.

Materials that have shown these properties include HOPG and single crystals of graphite, various polytypes of TaS_2 and $NbSe_2$, PbS(100) and possibly Au(111) [13] and Al(111) [14] (in the case of the last two the corrugation heights, measured in UHV, are typically a few tenths of an Ångström, surprisingly large for a close-packed surface). The property common to all (to a lesser extent the (111) metal surfaces) is the ease with which these materials can shear parallel to the surface presented to the STM tip.

In addition to the observations mentioned above which indicate contact, recent work by Mate *et al* [15] suggests that loads of greater than one micronewton are needed before current will appear across the biased STM junction of HOPG in air. This they ascribe to an insulating layer on the graphite surface.

Following up an earlier suggestion [16], we point out that if contact between tip and sample is demonstrable by mechanical measurement, then the imaging of periodic features in the STM can arise from oscillations in total conductivity occurring as the lattice planes just beneath the tip slide over each other. This gives a single cycle of conductance fluctuation for each lattice parameter moved laterally—'atomic resolution'. We discuss this model in more detail later. Colton *et al* [17] have shown that extended area tunnelling such as we have proposed can give the wide variety of repeated geometric features seen on graphite. Moreover, 'atomic resolution' images are readily obtained using a graphite tip. Further support for the model is given by the demonstration by Tiedje *et al* [18] of the spontaneous growth of carbon fibres on a metallic STM tip scanning HOPG. As mentioned in [16], the standard STM tunnelling theory for clean surfaces in UHV [19] assumes a tip diameter corresponding to a single atom. This fails to account for the stresses in a monatomic contact with the sample surface [20]. It has been suggested that a larger area of the tip can make mechanical contact mediated by insulating contaminant. The tunnelling is then via a single-atom tip protruding through this layer [12]. However, this is likely to be an unstable structure when the single atom and its neighbours undergo shear over a large number of lattice parameters.

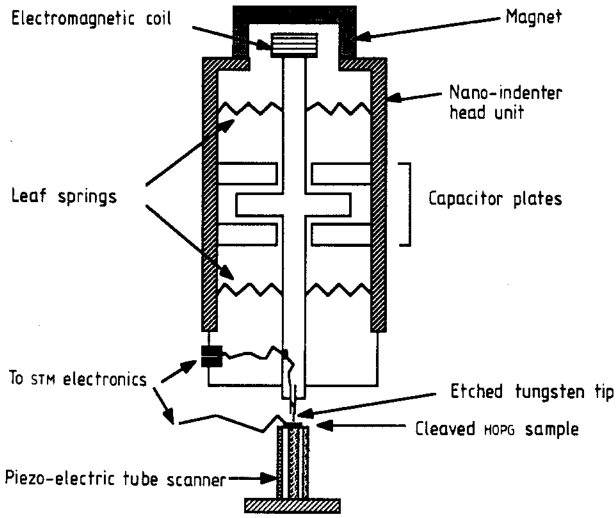


Figure 1. The nano-indenter as modified for STM.

In order to investigate the sliding planes model further, we have combined a load-controlled 'nano-indentation' device together with an STM sample stage and electronics, enabling us simultaneously to obtain both mechanical and electronic characterisation of surface contact in air.

3. The nano-indenter as STM

The experimental apparatus is shown in figure 1. An electrochemically etched tungsten wire, 0.4 mm in diameter, with a tip radius on insertion of less than 1 μm, was placed in the holder of the nano-indenter, with an electrical connection to the STM electronics. The holder is mounted in the identer head unit on a shaft connected to two leaf springs, whose total stiffness was 48 N m^{-1}. By means of an electromagnetic coil fixed to the shaft and a concentric magnet in the head unit, a force can be applied to the shaft, allowing controlled motion towards the sample at a speed of 5 nm s^{-1}. Displacement measurement is sensitive to a few tenths of an Ångström. Details of the nano-indenter are described elsewhere [21]. The sample, chosen to be HOPG (probably the most extensively studied material in STM), was mounted using epoxy resin onto a 1 cm diameter 'tube scanner' of the piezo-electric ceramic PZT-5A. The base of the tube was glued to a holder screwed onto the x–y table of the indenter. Thus the sample could be moved in three dimensions under the tungsten tip using the STM electronics, which were connected such that a bias voltage was applied to the tip, and current was collected from the sample.

A small AC modulation of the load was applied simultaneously with the STM imaging. Synchronous detection of the resulting AC displacement gave a measurement of contact compliance and hence area [3]. The modulation applied gave an oscillation amplitude of 0.5 Å.

Using the nano-indenter configured in this way we have the opportunity to attempt to image some of the familiar structures seen on HOPG (see figure 2 for an image from our standard STM), while simultaneously recording load, displacement and contact

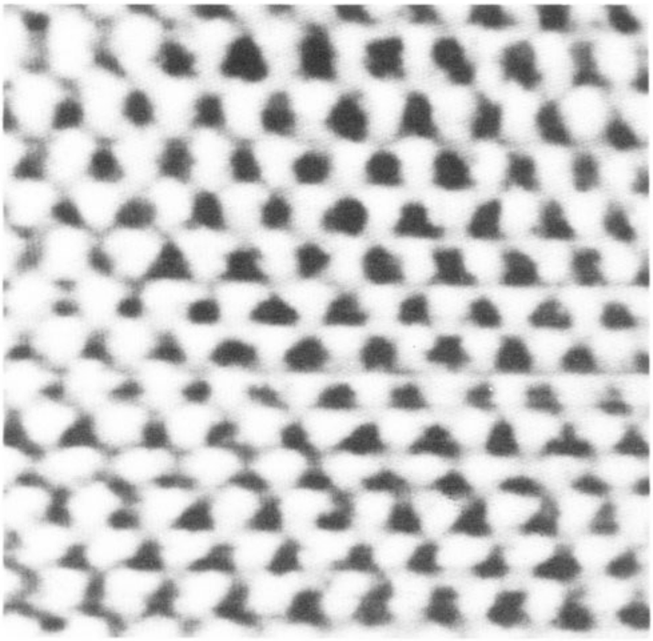


Figure 2. Typical grey-level STM image of HOPG. The data exhibit one of the anomalies of STM imaging; with a height difference between black and white of about 10Å, these are giant corrugations.

compliance to find at what contact area and under what load this shear-induced corrugation in current through the contact exists. This information is relevant both to STM and also to atomic force microscopy (AFM). AFM force sensitivity, typically 1 nN, far exceeds that of this indentation device. If 'atomic resolution' pictures can be obtained with the relatively crude nano-indenter, then a robust mechanism of contrast such as we propose is certainly necessary.

4. Results

4.1. Mechanical and electrical properties of HOPG

Highly oriented pyrolytic graphite is unusual both in its electronic and its mechanical properties. To explain the anomalously large amplitude of corrugation in STM scans others [11, 12] have shown that contact, perhaps mediated by non-specific contaminant, is the most likely cause. The key question is whether we are seeing atomically localised tunnelling at all in such cases (possibly via a micro-tip protruding through the insulating layer), or whether instead contrast in the image arises by averaging over a larger area than the apparent resolution suggests.

Mechanically too, HOPG behaves in special ways. Micrometre-sized depressions made with a triangular diamond indenter, which are visible under a high magnification light microscope, do not generally show the characteristic triangular shape, and the load versus displacement curves were found to give greater scatter than for uniform materials

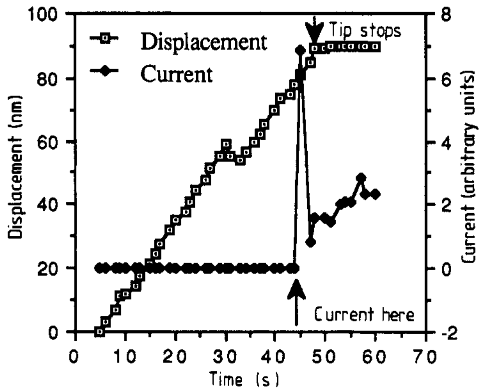


Figure 3. Incidence of electrical and mechanical contact. The load was increased steadily throughout.

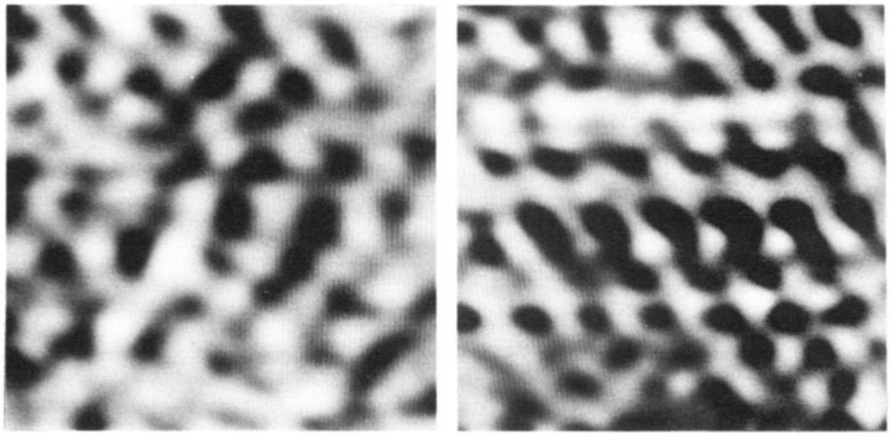
such as tungsten. It may be that the tip breaks through the material in sudden jumps, possibly picking up flakes as it does so and making the process irreproducible.

Switching from a diamond tip to the tungsten tip made it possible to compare the time at which the tip and sample could be considered to be in contact, from both mechanical and electrical measurements independently; we could compare the load–displacement data or a phase change on the compliance-sensing lock-in amplifier (for details of this method see [3]) with the onset of current from the sample. The current usually appeared before the lock-in change (see figure 3). This might imply that the surfaces are rather clean, but caution is needed about possible flakes. In some cases, however, the onset of current followed the mechanical contact, and with low bias voltages current failed to appear even with the tip hundreds of Ångströms into the surface. This delay must be due to contamination , which therefore varies significantly over the surface.

4.2. Imaging in contact

The best images exhibiting the contrast of the surface at the atomic scale are given in figure 4. The periodic structure is clearly visible, with no image enhancement. The bias voltage of 10 mV gave a current of approximately 10 nA. Both images were obtained at 10 Hz scan rate, and in definite contact; the load was such that the lock-in phase had moved from 21 degrees with the tip clear, to 45 degrees. This corresponds to a stiffness greater than 40 kN m^{-1}. Periodic structure on the atomic scale is definitely seen. Its spacing is not dependent on scan speed. The 'amplitude' corresponds to 10% current modulation. No feedback was used to stabilise the tip in these images, as the current was steady to within ten per cent. In some cases where a stable current flowed, the AC modulation showed no change in phase from the approach value—it is probable that there is then a high compliance conducting path through a small flake, so no images were taken in these cases as we wished to be certain of mechanical contact.

Several unusual but reproducible phenomena appeared during the course of the experiment. There were some approaches where no current was seen unless a bias voltage of over 3V was used. Switching from low to this higher voltage apparently causes an opening of a new conductance path or breakdown, with a characteristically stable



(a) (b)

Figure 4. Images taken with the hybrid nano-indenter/STM on HOPG with tip–sample contact, as determined by compliance change.

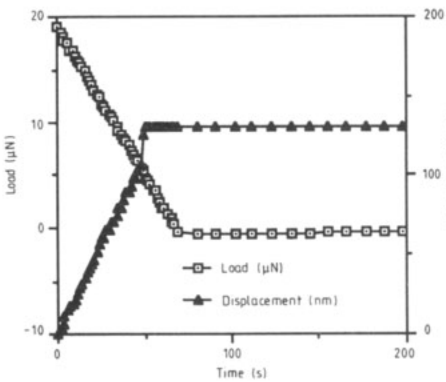


Figure 5. Approach data showing jump into contact. Adhesion on withdrawal was also seen; from just making contact, the tip had to be moved up 100 nm to break contact.

current, unchanged by moving the tip through hundreds of nanometres. This seems to imply that the surface was dirty. The voltage change was accompanied by a movement of the tip towards the sample on switching to high bias.

In a few approaches the tip seemed to jump towards the surface from perhaps 100 Å away. On unloading, the position at which electrical contact was broken was higher than that at which current had first appeared, suggesting adhesion between tip and sample. Figure 5 gives an example of this effect.

5. Can layer shearing give the measured current fluctuation?

Consider a small-area shear, like that shown schematically in figure 6 (note that in practice elastic shear of the adjacent lattice will also occur; we focus on the plane that shears inelastically). We are not aware of any quantitative modelling of conductance

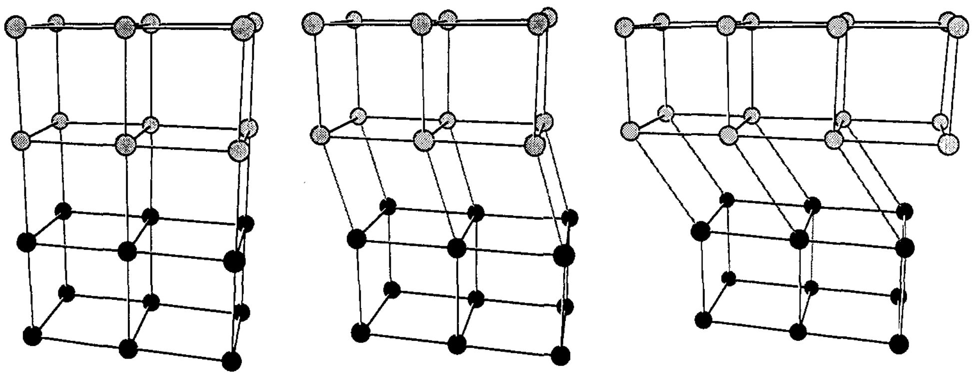


Figure 6. Schematic sequence of positions for the shear model. In (*a*) the upper and lower lattice line up. The lattice mismatch as they slide relative to each other in (*b*) and (*c*) gives rise to scattering and hence increased resistance. In reality the shear will take place over several planes.

through this geometry, so to estimate whether the mechanism is capable of giving the contrast required for STM imaging, we make a simplifying assertion: as the lower section of the lattice moves in and out of registry with the upper section, a scattering interface appears between upper and lower lattices; we suggest that this can be treated like a grain boundary which sequentially appears, intensifies and diminishes again. It then becomes a question of assessing the resistance due to a section of grain boundary, for comparison against the typical ten per cent fluctuations in tunnelling current that we observe when imaging graphite in the variable current (fast scan) mode. Andrews *et al* [22] measured a 'grain boundary specific resistivity' (resistivity due to grain boundaries/grain area per unit volume—call it S) by measuring the resistance of pure single-crystal metals compared with their polycrystalline forms. His result for copper of $10^{-16}\ \Omega\mathrm{m}^2$ agrees with a recent pseudopotential calculation by Lormand [23]. In our case then, the additional resistance due to a quasi-grain-boundary at the sliding interface with circular cross-section of radius a is simply $S/\pi a^2$. Comparing this with the Maxwell resistance, given by $r/4a$, where r is the resistivity, we conclude that the ratio of resistances between perfect alignment and misalignment, corresponding to the contrast in our images, we will be given by

$$C = 4S/\pi a r.$$

For copper, this implies a contact diameter of 160 nm for a contrast ratio of 10%. This is a contact of considerable size, and smaller contacts will be capable of even stronger contrast. It is clear from this that quite sufficient scattering is available at the shearing interface for the imaging mechanism we are suggesting. If the contact radius is smaller than the mean free path (λ), then the Sharvin formula for resistance, $4r\lambda/3\pi a^2$, will apply. In this case

$$C = 3S/4r\lambda$$

and the contrast becomes a constant value. The implication is that for very small contacts, the image contrast will be very stable, being relatively independent of changes in area. This may partly explain why very clean images of graphite are so easily obtained.

The above calculation is for copper. In the absence of values of S for graphite (particularly if intercalated near to the surface), it seems reasonable to assume that grain boundary resistance scales with resistivity itself, and hence the above order of magnitude estimates are reasonable. In any event, quite sufficient contrast is clearly available, and the implied conducting contact areas are of the same order as those experimentally observed. We note that the process of sliding may well be incoherent at large contact areas; the phenomenon may therefore only be observable in point contact or in similarly constricted geometries.

An alternative to the mechanism implied by figure 6 is the movement parallel to the surface of a single dislocation in the region of contact, acting as a scattering centre for conduction electrons. If the contact area is sufficiently small the passage of each dislocation through the constriction introduces a single scattering centre per lattice parameter of shear, which can again give periodic contrast to the image as the tip is rastered across the surface.

6. Implications and conclusions

A number of important conclusions follow from our model. First, the model may also be relevant in metals, especially on the low shear stress planes (for example (111) FCC or basal plane HCP). This could explain the most surprising features of the images obtained on Au(111) and Al(111)—the regular, enhanced corrugation. The 1MΩ resistance observed by Hallmark and co-workers [13], while larger than that expected in point contact, is considerably lower than typical STM values of 1GΩ. The present crude picture does not include the possibility of insulating material between tip and sample, and imprecisely forecasts the properties of a scattering interface in a constricted geometry. We are currently investigating a more detailed model.

The approach could also provide a means of making quantitative observation of the scattering amplitude arising from single-atom defects, an effect that may even be quantised. In addition it illustrates the existence of novel phenomena in mechanics at the near-atomic scale, indicating block shear (which is likely to be near or at the theoretical lattice strength), and the possibility of discrete frictional forces. These processes have in fact recently been observed [3, 15]. A general feature of the investigation of nanometre scale volumes and surfaces is that more 'pure' phenomena are observable, because the scale is below that of the co-operative or consecutive processes which generally dominate macroscopic properties.

In summary, we have proposed an imaging mechanism for STM on materials having low critical shear stress planes. Using a device for measuring mechanical properties on the nanometre scale, we have investigated the behaviour of tip and HOPG sample in air and found evidence of atomic scale imaging in definite contact. The current fluctuations are consistent with an order of magnitude estimate based on modelling the shear interface as a grain boundary. Our model explains a considerable variety of otherwise unrelated but curious aspects of STM imaging of these materials. We have concluded with projections based on the implications of this model.

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