Conducting-Probe AFM Nanoscale Joule Heating Yields Charge-Density-Wave Transition Detection

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Several layered transition-metal dichalcogenides are studied using conducting probe AFM aiming to investigate the probe-mediated thermal processes likely to arise in the probe−substrate vicinity due to the high-current densities involved. A signature of local heating is found in the shape of current−potential (i/V) curves. The latter allows straightforward detection of a charge-density-wave (CDW) transition for 1T-TaSe$_2$ samples exhibiting it above room temperature. This is an illustration of a new use of conducting probe AFM to investigate solid-state bulk characteristics owing to a distinctive nanoscale Joule heating.

1. Introduction

Due to the very large current densities implicated in STM and in conducting probe (CP)−AFM, substantial local Joule heating is likely to arise in the probe−substrate vicinity, and indeed, several prospective applications based on this nanoscale phenomenon have been investigated. Early results, obtained by STM operating in ambient air, involved the creation of gold nanopatterns,[1] and the mechanism was believed to be an intense local heating due to the current densities involved. However, the expected corresponding temperature rise, ΔT, was estimated later by others[2] to be exceedingly low ($\Delta T < 1$ K). Apart from few reports,[3] subsequent studies corroborated a negligible temperature elevation by tunnel-current mediated Joule heating. Alternate physical mechanisms controlling these processes, e.g., tip/sample contacts,[4a] or local melting of the tip due to the Nottingham effect,[4b] have been suggested, as well as the possible incidence of some nanoscale-inherent heat conduction mechanisms.[4c]

However CP−AFM investigations yield less conflicting results in this area. Sub-μm fabrication of transistor structures by thermally assisted electro-migration of mobile dopants,[5] thermo-mechanical polymer lithography[6] as well as nanoscale creation of marks in phase-change media,[7] have been unambiguously assigned to thermal processes mediated by tip-to-substrate current Joule heating. The currents involved in CP−AFM (usually up to about 0.1 mA range[8]), and as a consequence, the injected powers[9] are several orders of magnitude higher than STM currents (nA to μA range). Therefore, using the following standard steady-state solution to the heat flow equation: $\Delta T \approx (P/l.k)$ (where k is the thermal conductivity of the material, l stands for the tip contact-radius, and $P = $ I.V is the power input), estimations of the temperature-rise ΔT obtained by CP−AFM are in the range of 100−800 K,[5,7b,c] depending on the thermal conductivity k of the materials considered.

Previous investigations involved exclusively isotropic solids, whereas interesting effects might be expected with anisotropic materials for these nanoscale thermal processes. Considering a simple uniaxial anisotropy, involving two main thermal conductivities k_r (in-plane) and k_z (in the perpendicular z direction),[10] we derived a corresponding solution to the heat diffusion equation. We find, for a power input P at a contact-radius l on the (x−y) plane, a temperature increase in the steady state at the center of the contact area: $\Delta T \approx (P/l.\sqrt{k_r k_z})$. Clearly, this implies that a noticeably higher local temperature could be reached in an anisotropic (e.g., layered) solid, with the same injected power P (compared to the formula above), as long as a significant k_r/k_z ratio arises *mainly* from a decrease of k_z. Therefore, we have selected several 2D anisotropic conductors in the layered transition metal dichalcogenides series, aiming to investigate probe-mediated thermal processes in more detail. We report here the results of a CP−AFM investigation of 1T-TaS$_2$, 1T-TaSe$_2$, and 2H$_a$-TaSe$_2$ single crystals,[11] emphasizing an unexpected aspect of these nanoscale Joule heating processes. We find a signature of local heating in the shape of current−potential (i/V) curves, which allow a straightforward detection of a charge-density-wave (CDW) transition for samples exhibiting the latter above room temperature.[12]

2. Experimental Section

2.1. Materials. The tantalum dichalcogenide single-crystals were prepared according to the literature.[11] As described in these procedures: (i) TaX$_2$ (X = S, Se) powder samples were prepared from mixtures of 99.98% pure tantalum and 99.999% pure sulfur or selenium; a slight excess of chalcogen over the required stoichiometric amount (0.1−0.2%) was used and the mixtures left over three weeks in evacuated (to 10^{-3} mbar) quartz tubes at 1123 K for 1T-TaS$_2$ or 1173 K for 1T-TaSe$_2$ and 2H$_a$-TaSe$_2$, respecitvely, after setting an adapted warming-up program to control the stoichiometry and the sample crystallinity; and, (ii) the single crystals were produced by vapor phase transport with an iodine transport agent in a 50 K temperature gradient around 1150, 1100, and 1200 K for, respectively, 1T-TaS$_2$, 2H$_a$-TaSe$_2$,

* Corresponding author E-mail: moradpour@lps.u-psud.fr.
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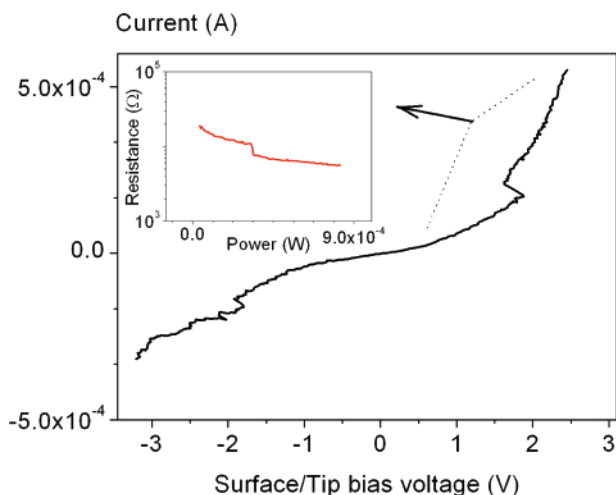**Figure 1.** A current-potential curve obtained for 1T-TaSe$_2$ single crystals in ambient air at scan-rate of 30 V.sec^{-1}; the potential is scanned from 0 to 3 V, and subsequently from 0 to -3 V. The insert shows a portion of the scan plotted as contact resistance (V/I) vs power input (V.i) and highlights a resistance drop as a function of the power input.

and 1T-TaSe$_2$, and subsequent quenching above 1173 K (1T-phases) or around 850 K (2H$_a$-TaSe$_2$) after a three week growth-period.

2.2. Atomic Force Microscopy Measurements. The measurements were carried out using a CP−AFM instrument, equipped with diamond-coated Si cantilevers (Nanosensors, spring constants ≈ 2N/m). The AFM instrument (Nanoscope III, Veeco) includes a homemade system for local contact-resistances and current measurements (Resiscope).[8] This specialized setup accounts for the specific shape of the i(V) distortion related to the sudden contact-resistance decrease observed with CDW-involving materials (see the Supporting Information for details).

3. Results and Discussion

The experiments were performed in ambient air on freshly cleaved single crystals. A typical probe-to-crystal current−potential wave obtained with 1T-TaSe$_2$ is shown in Figure 1. Around +2 V (and −2 V) bias voltage distinctive distortions, highly reproducible *at different locations,* are detected in the (i/V) curve. At this stage, we suggest that these distortions might be due to the CDW transition exhibited by this layered compound 1T-TaSe$_2$.[13] The resistivity of this solid is known to drop abruptly at the transition temperature ($T = 473$K), from 2500 Ω.cm (low-temperature phase) to 500 Ω.cm (high-temperature phase).[13a] If this transition temperature is reached locally by probe-mediated heating, the corresponding resistivity-variation will strongly affect the probe contact resistance, and might generate the distortions detected in the (i/V) curves. Indeed, plotting the (i/V) data as V/i versus V.i clearly indicates that a change in resistance is involved as a function of input power (Figure 1, insert). We also find that (i) as corroboration of a thermal origin, the incidence of the distortion is independent of the potential scan-direction (Figure 1),[14] (ii) it is interestingly suppressed when a dry air (or dry nitrogen) flow is maintained in the sample compartment (Figure 2A). When a gas flow is present, the inhibition of the (i/V) distortion reflects the fact that the transition-temperature is no longer reached, due to more efficient cooling of the sample.

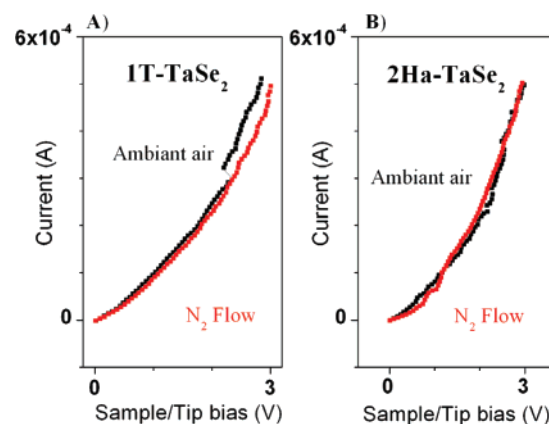To corroborate these assumptions, we examined the 2H$_a$-TaSe$_2$ polytype devoid of such a high-temperature CDW

Figure 2. (a) 1T-TaSe$_2$ scanned from 0 to 3 V in ambient air (in blue) and under a dry nitrogen flux (in red) (≈0.5 l.min^{-1}); (b) 2H$_a$-TaSe$_2$ scanned in ambient air (in black) and under a dry nitrogen flux (≈0.5 l.min^{-1}) (in red).
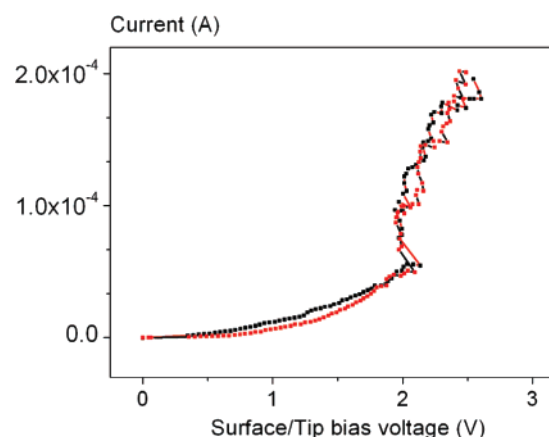

Figure 3. Two repetitive scans involving 5 min scan intervals recorded at the same contact point.

transition.[13b] As can be seen (Figure 2B), no more distortion is observed in the (i/V) diagram of this solid.[15]

The reversibility of this (i/V) distortion, that would unambiguously demonstrate the involvement of a reversible CDW phase-transition, was investigated. The same contact point was repetitively scanned, in the voltage range of 0−3 V[16] with time intervals of about five minutes between each scan to allow probe−substrate cooling. Nearly identical (i/V) distortion is obtained for each such delayed scan (Figure 3).[18] Further on, the experimental parameters controlling this (i/V) distortion, as signature of a thermally induced contact-point sudden resistance change related to a CDW transition were investigated. The dependence of this distortion on the voltage scan rate was first considered.

Lowering the potential scan-rates involves significant shift of the distortion to (almost 1 V) lower potentials (Figure 4). This behavior might be rationalized considering, for each scan, the total energy input involved in periods of time ending when distortion occurs. In view of the investigated current−potential and scan-rate parameters (Figure 4), the total energy input corresponding to the lowest scan rate (2 V.sec^{-1}; scan duration: 1.7 s) is estimated to be almost 10 times higher than that of the fastest one (90 V.sec^{-1}; scan duration: 0.04 s)). Therefore, bearing in mind the rather poor thermal conductivity of the present layered material[19] (see the the cooling delays for the repetitive scans above), or in other words, roughly overlooking the heat leaks, the lowest potential scan-rate run (2 V.sec^{-1}) involving a *larger injected energy*, accounts for the nanocontact reaching the transition temperature at a lower potential.
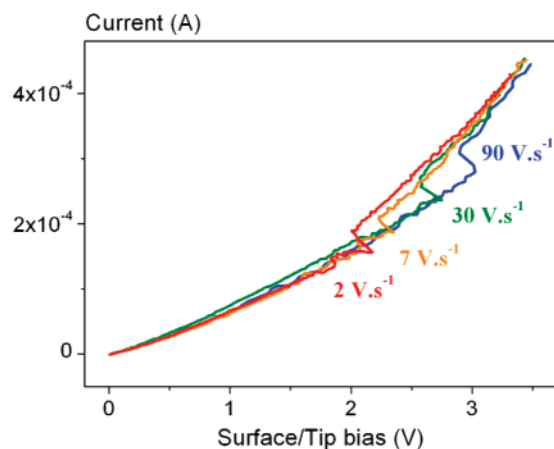
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Figure 4. The potential scan-rate dependence of the 1T-TaSe$_2$ CDW-transition detection.
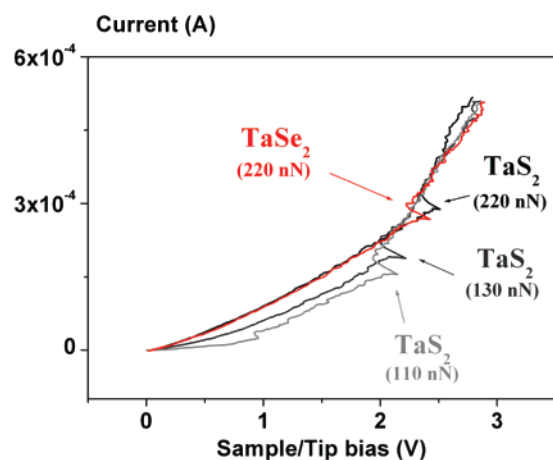

Figure 5. Current-potential curve of 1T-TaSe$_2$ (in red) compared to 1T-TaS$_2$ (in black, recorded with the same 220 nN contact-strength) in ambient air at potential scan-rate of 30 V.sec^{-1}; the influence of the cantilever contact-strength modulation on 1T-TaS$_2$ curves (to 110 and 130 nN) is shown in (dark and light gray).

Whether any temperature calibration of the potential axis is possible was, therefore, subsequently examined. For this reason, (i/V) curves of 1T-TaS$_2$, a layered conductor exhibiting a similar CDW transition at a lower (348 K) temperature[11c], were compared to those of 1T-TaSe$_2$ (Figure 5).

However, despite a 125 K lower critical temperature, the corresponding distortion was found at a somewhat higher potential!

We clarified this unexpected result by modulating the cantilever contact strength. Significant potential-shifts (up to almost 0.5 V) for the distortion of 1T-TaS$_2$ (i/v) curves result from contact strength modifications from 110 to 220 nN (Figure 4). The cantilever contact strength controls the contact area and consequently the current density. These potential shifts, therefore, emphasize the important effect of the contact area, or in other words the important effect of the current density, consequently strengthening again the thermal origin of (i/V) distortion. Going back to the 1T-TaSe$_2$ vs 1T-TaS$_2$ evaluations, we assume that, despite similar contact strength (220 nN), the contact areas might be appreciably material-dependent, and therefore, significantly different for these two solids. This emphasizes that an exact temperature-calibration is, unfortunately, not yet presently achievable, still the considered sample/tip local heating temperature range can be evaluated to exceed 500 °C[16,17] for the highest potential values reached (8 V).

4. Conclusions

In summary, the results demonstrate an, as yet unreported, way to detect a CDW transition above room temperature by CP−AFM through variation of the probe−substrate nano-contact(i/V) characteristics due to local Joule heating. This is an illustration of an, as yet uninvestigated, use of CP−AFM as a means to investigate solid-state bulk characteristics owing to a distinctive nanoscale feature.

Supporting Information Available: Current-potential curve scanned up to 8 V for 1T-TaSe$_2$ single crystals in ambient air at a bias scan-rate of 4V.sec^{-1}, and the resulting insulating spot obtained on the initially highly conducting crystal surface; details on the surface modifications of 1T-TaSe$_2$ obtained in ambient air at 8V, as compared to modification with exclusion of oxygen (nitrogen flow); account of the voltage discontinuity of the i(V)curves given by the "resiscope" for materials involving a thermally induced sudden contact-resistance variation. This material is available free of charge via the Internet at http://www.pubs.acs.or

References and Notes

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(14) Apart from the experiment shown in Figure 1, obtained on the first scan (with a probe subsequently damaged on the next), potential scans in the opposite direction were not attempted because of very fast probe-degradation as already reported, see ref 8.

(15) Phenomena related to boiling at the considered temperatures (removal) of the water meniscus existing at the probe-substrate contact (even

under dry nitrogen flows[8]) could have been considered as a possible account for the 1T-TaSe$_2$ (i/V) distortion. However, the 2H$_a$-TaSe$_2$ polytype free-of-distortion behavior completely excludes the involvement of such phenomena.

(16) It is worth noting that the i(V) curves from potential-scans extended to higher potential values (8 V) in ambient air, exhibit a sharp current decrease resulting from a chemical process related to an irreversible surface modification,[17] involving the formation of an insulating dot (see the Supporting Information for: (i) a current−potential curve obtained for 1T-TaSe$_2$, scanned from 0 to 8 V, and the corresponding insulating dot, and (ii) a similar surface-modification phenomenon for larger areas scanned at 8,V; remarkably, when the scans are performed with exclusion of oxygen, the formation of such insulating areas is no longer observed, indicating that a local oxygen-dependent thermal decomposition process indeed occurs in ambient air (over 500 °C) at the probe-substrate contact point).[17]

(17) The onset temperature of the thermal decomposition of TaSe$_2$ in dry air has been determined to take place over 500 °C.; see: Lavik, M. T.; Moore, G. D. *Lubr. Eng.* **1967**, *23*, 224.

(18) If the probe-substrate contact point is not allowed to cool, the local heat and temperature increase prevent the detection of an i(V) distortion. Thus, *un-delayed* reverse-direction potential scans do not generally exhibit i(V) distortion.

(19) It should be noted that serious heat leaks at the contact point, either at the probe or the sample, is undesirable and inhibit the present i(V) distortion. In fact, the CDW is no longer detected if metal-coated (i.e., Pt/Ir coated) cantilevers are utilized instead of the present diamond-coated Si cantilevers. In other words, using suitable probes, the ability of the method is ultimately restricted to the examination of poorly thermally conductive materials.