Reply to "Comment on 'Current routes in hydrogenated microcrystalline silicon' "

D. Azulay,[1] I. Balberg,[1] V. Chu,[2,3] J. P. Conde,[2,3,4] and O. Millo[1]
[1]*The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel*
[2]*INESC Microsystemas e Nanotechnologies, IN Istitute of Nanoscience and Nanotechnology, Lisbon 1000-029, Portugal*
[3]*Department of Chemical and Biological Engineering, Instituto Superior Técnico, Lisbon 1049-001, Portugal*
[4]*Department of Materials Engineering, Instituto Superior Técnico, Lisbon 1049-001, Portugal*
(Received 2 July 2009; revised manuscript received 7 January 2010; published 4 June 2010)

The comment of Vetushka *et al.* [Phys. Rev. B **81**, 237301 (2010)] represents a conductive atomic force microscopy study of μc-Si:H. The observed higher conductivity at the known columns (grain) edges was suggested to reflect an oxide buildup that is due to a tip-surface contact effect. The commenters further suggest that this is also the case in our observations that we interpreted to be due to the relatively high conductivity of these edges. Taking many and detailed precautions, including all those proposed in the comment, appears to indicate that at least in our samples our original interpretation is valid. This interpretation is strongly supported by our current imaging tunneling spectroscopy study in which no tip-surface contact effect exists.

DOI: 10.1103/PhysRevB.81.237302 PACS number(s): 73.50.Pz, 68.37.Hk, 68.37.Yz, 72.20.−i

The comment of Vetushka *et al.* (hereafter the "commenters") represents a conductive atomic-force microscopy (C-AFM) study that revealed an effect that applies to samples of hydrogenated microcrystalline silicon (μc-Si:H) that were prepared and studied by their group. Referring to our previous work,[1] the principal statement in their comment is: "we conclude that even in their case the conductive rings were actually an artifact resulting from the tip-induced oxidation." The consequence of their comment is then that: "the observed higher conductivity at the grain edges reflects a state of the surface of the sample and it cannot be used for arguing about the transport route within the material itself." The above statements imply then that the commenters consider their conclusions as "universal" for the μc-Si:H system. Consequently, the comment may cast doubts concerning the dominant current network that consists of the disordered columns encapsulating tissues (CETs) (Refs. 2 and 3) as we concluded from our microscopic[1] and macroscopic[4] studies. Indeed, our C-AFM study[1] yielded results that are in contradiction to the previous conclusion of the commenters[5,6] who suggested that the dominant current takes place via the interior in the columns.

As the latter works preceded ours we were aware of the contradiction between their results and ours, and we took proper precautions (see Ref. 1 and the details to be given below), and discussed the possible reasons for this contradiction in our paper[1] with which the comment is concerned. The basic reason that we suggested for the opposite observations was the more pronounced oxygen-induced doping in our samples in general[7–10] and in the CETs,[7,8] in particular. The comment of Vetushka *et al.* tries to refute our interpretation that is based on differences in the material studied by the two groups. Correspondingly, we will show below that our experimental results do indeed differ from theirs and then discuss the possible interpretation for the differences in the observations of the two groups. However, before summarizing our results and our suggested interpretation let us make a few remarks to set the stage for our reply with respect to the comment.

(1) The claim made in the comment that "the conditions of the scan presented in Fig. 3 were identical to the conditions used in Ref. 4" is far from describing the real situation in the present context since, as in such cases, not all the details of the measurements and the *sample preparation* are given in the papers and, in the present case, some significant differences are even explicitly apparent. For example, we did not use only a +10 V scans (such as the results shown in Ref. 1) but also conducted many scans with V values in the +2.0 to +10 V range as well as in the −2.0 to −10 V range, finding no differences in the features of the images. In particular, the statement that the sample was first scanned with a high oxidizing voltage (+10 V), "same as in Ref. 4" does not apply. In fact, while not detailed within the brief framework of our paper[1] we performed our measurements under several bias voltages in both polarities while starting a series of scans at a new location with different voltages (negative or positive, low or high), finding, that all the scans showed that the CETs are more conductive. Furthermore, we have performed several sequences of measurements with the same conditions on the *same* location and *did not notice* any changes in the current maps—meaning that there is no evidence for the tip anodic oxidation effect as specified in the comment. In addition no "steps" were observed in the topographic images that could be related to the formation of an oxide layer. Therefore this comment cannot be applied to our measurements. Also, the implication that their samples and ours were prepared under similar "standard" conditions is also unfounded, as can be seen by comparing the details that were given in Ref. 1 and in the comment. One apparent example of such a difference is the type of sample growth that may result due to the different substrates used in the two studies. This may affect, in particular, the degree of crystallinity, the evolution of the columns, the porosity and in turn also the efficiency of oxygen intake. More significant for the context under discussion is their rather indefinite statement that in their samples the oxygen content is "as low as state-of-the-art thin film Si." The fact that it is not quantitative for the samples used in the comment (in particular, secondary-ion-mass spectroscopy, has not been reported by the commenters group) does not enable an explicit comparison with our samples for which the oxygen content was explicitly given (a few times 10^{18} cm^{-3}). In fact, this statement and

 ©2010 The American Physical Society

other indications (that will be mentioned later) imply that their samples have relatively low oxygen doping in comparison to our samples in accordance with our explanation[1] for the different behaviors found in the two studies. This is an important difference since it is well known that the amount of oxygen content (that is present in the CETs) greatly influence the conductivity. In particular, it is well known that the deposition[7] and post deposition[8] conditions, such as different atmospheres, deposition rates, and substrate temperatures, in general, and in the presence of the columnar structures,[8] in particular, may determine the dominant role of the oxygen on the transport. This is since the oxygen may act as a dopant as well as an oxide builder in μc-Si:H. Indeed, it was shown in[11] that "unless special precautions are taken the measured data can be significantly influenced by incorporated oxygen." In fact, Ref. 11 showed that a "decrease and recovery of the electrical conductivity due to oxygen exposure and annealing" are possible. Following that, it may be well expected that the differences in the sample preparation conditions, that are or are not explicitly reported, are more than enough to account for the differences in the oxygen content and its doping effect in the films that were used by the two groups, thus yielding the different observations, as we suggested originally.[1]

(2) The oxygen has not only a role in the building up of a "surface-insulating layer" but has also the role of the oxygen as an effective donor dopant in the μc-Si:H system,[7,10] in general, and in the CETs, in particular.[8] In fact the oxygen doping in hydrogenated amorphous silicon (a-Si:H) (Ref. 12) (discussed in numerous papers) as well as the well-known gettering effect of various impurities, including oxygen, in polycrystalline silicon[13] are also well known. In particular, we note that in Ref. 11 it was concluded that "the nature of the Si-O sites in a-Si and on the grain boundaries in nc-Si structure is similar" (note that nanocrystalline silicon, nc-Si, stands there for μc-Si:H). As pointed out above this higher oxygen content in the CETs, in comparison with that in the crystallites, may be different in differently prepared samples as it depends on the deposition and post depositions conditions.[13]

(3) It should be further noted that small differences in the deposition and post deposition conditions result in very different effects, not only on the oxygen doping mentioned above but also on the very process that they suggest, i.e., the build up of the oxide on the surface. For example, a study carried out on polycrystalline silicon (PSi),[14] that is very similar to the study reported in the comment, *has shown the opposite surface oxidation behavior to the one suggested in the comment*, revealing more "efficient" oxidation at the grain boundaries. Hence, it is quite apparent that the interpretation of the results by the commenters is not the only possible one.

(4) The commenters statement that their "samples for the microscopic and macroscopic results are usually prepared in the same run" does not reveal whether indeed the samples used in Refs. 5 and 9, and in the present comment were prepared in the same run and kept under similar conditions afterwards. This is to be contrasted with the self-consistent picture that we derived by using the very same samples for both our macroscopic[4] and microscopic[1] measurements.

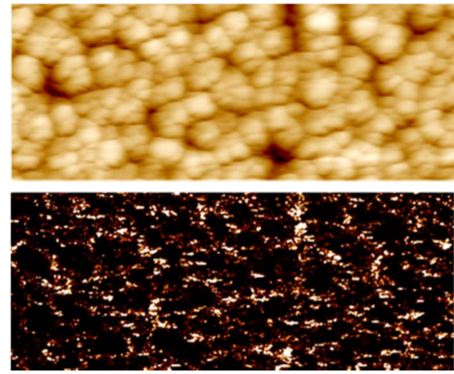

FIG. 1. (Color online) 2×0.8 μm^2 topography (upper panel) and current (lower panel) images measured on an etched sample (using 10% diluted HF) at a bias of +5 V. Current scale: 0–15 nA.

Turning to the experimental findings we noted already above that since the previous works of the commenters group[5,6] preceded and contradicted ours, we carried out a comprehensive, systematic, and rather tedious study in order to confirm that our results are not an artifact of the measurements.[1] In particular, we took quite a few precautions and performed various procedures, including, already then,[1] *all the "litmus tests"* that the commenters suggest now, for eliminating or avoiding "artifacts." For example, the commenters suggest that "the oxidation artifacts in μc-Si:H local current maps can be avoided by not using high positive sample voltages." Then, they state that "furthermore we have successfully tested a simple procedure for removing the oxide from the surface of the silicon films: samples were put into 10% water solution of HF for a few seconds, rinsed by deionized water and blown dry by an air jet. This procedure restored the local current values and features comparable to those measured by C-AFM in UHV on in situ prepared samples. Hence this procedure can be easily used to verify C-AFM results even on aged samples." (Here HF stands for hydrofluoric acid and UHV for ultra-high-vacuum.) Indeed our measurements were carried out before and after a diluted HF etching of some of the samples and we performed the C-AFM scans under the two fast-sweep opposite directions and under the two bias polarities, with various voltages, and using various conducting tips (in the −10 to +10 V bias range) in the two fast-sweep opposite directions. Such a typical image taken then on an etched (10% diluted HF) sample for a bias of +5 V is shown in Fig. 1, revealing clearly that the current takes place through the CETs. Similar results on an unetched sample that were obtained under a nonoxidizing negative bias (−3 V) application are shown in Fig. 2. Furthermore, in order to eliminate, in particular, the *a priori* possible tip-sample surface oxidation effect due to the ambient (or humidity) we have carried out the measurements not only in an ambient atmosphere (using our NT-MDT apparatus) but also under ultra-high-vacuum conditions (using a variable temperature UHV scanning tunneling microscope/AFM Omicron system). *All these measurements revealed no significant differences and, in particular, in all of them the dominant current was via the disordered CETs that encapsulates the columns.* Hence, even according to the commenters, these procedures should have secured the elimination of at-

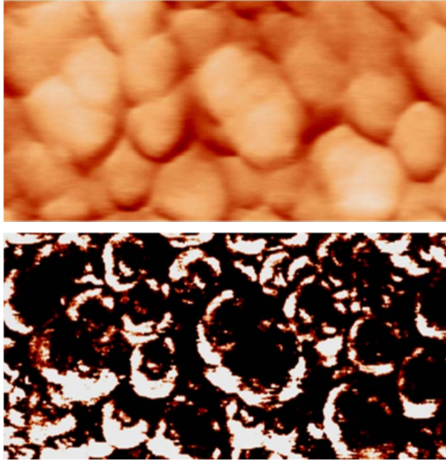

FIG. 2. (Color online) 0.6×0.3 $\mu\mathrm{m}^2$ topography (upper panel) and current (lower panel) images measured on an unetched sample at bias voltage of −3 V. Current scale: 0–15 nA.

tributing our observations to the tip-sample anodic oxidation.

To eliminate any doubt, if such still remains after all the procedures that we took, we have applied the scanning-tunneling-microscopy-based current imaging tunneling spectroscopy (CITS) technique (which is detailed in our Ref. 15), showing (see Fig. 4 in Ref. 1) again that the dominant current is via the above tissues. *This result cannot leave any doubt that the mechanism suggested in the comment for the artifact does not apply in our study, as this CITS method is a contactless method and as such, the tip-surface oxidation effect proposed in the comment is irrelevant.* To explain this very apparent contradiction with their interpretation the commenters state that "a lot of things could lead to the observed current traces." However, this is too indefinite. In fact we cannot respond to this remark since no CITS images were presented in the comment or in other publications of the commenters. In contrast the reader can see that our results as given in Fig. 4 of Ref. 1 are very conclusive. We suggest that assuming that their CITS measurements were properly performed the "inconclusiveness" of their CITS study is simply a result of the very low conductivity of the CETs in their case as is apparent from the orders of magnitude larger currents that we observed and they did not. Also, the commenters mention that our CITS were only performed on the $x=1$ phase. This is directly related to the fact that such a sample has a high conductivity (about three orders of magnitude larger than their samples) and can be therefore measured using the CITS.

Following the fact that we have established above that our experimental findings are different from those of the commenters we try now to suggest a possible explanation for the contradictions between the findings of the commenters and those of ours[1] as well as with the conclusions of the macroscopic studies of others[2,10,16] and ours[4] (in which tip induced effects are not present) that the conduction is dominated by the CITs. Before we start we note, as did the commenters in a recent work,[9] that "the role of oxygen is very complex and more research is needed." Hence, it is obvious that a comprehensive review of the effect of oxygen in Si systems is far beyond the scope of this reply. We also recall that the relevant oxidation effects that were studied, in particular, on polycrystalline silicon, are still a matter of controversy and that a unified picture of these processes has not emerged yet.[13,17,18] In particular, the oxidation processes were found to be very sensitive to the deposition and post deposition conditions and thus it is (in spite of the numerous works on the problem) *hard at present to pinpoint* what differences in the specific preparation conditions of the samples or their history are responsible for the different outcome in the oxidation process. In fact, opposite outcomes were reported for seemingly similar conditions, as can be seen by comparing the results of Ref. 14 and those of the commenters. The specific issue in the present problem can be summarized as follows. First, as realized recently also by the commenters,[9] the CETs (called large grain boundaries, LGBs, in Ref. 9) "consist of amorphous tissue into which the defects, together with hydrogen and probably oxygen atoms, concentrate." On the other hand, it was previously argued that no inhibition of columnar growth exists,[7] at least for the oxygen contents at the level that is present in our samples. Moreover, we note that in the a-Si:H samples that were deposited under the same conditions (except for the H_2 dilution) we found, from the macroscopic measurements, strong evidence for the high oxygen content (that was monitored directly and independently) as well as its importance in the transport.[19] However, even if the inhibition of columns argument is valid, the presence of columns is not an evidence for the absence of oxygen in the tissue since an intermediate situation of the presence of some oxygen and the presence of columns can occur. On the other hand, the role of oxygen as a donor is well established for crystalline silicon,[20] amorphous silicon,[12] and μc-Si:H.[21] Hence, there is a strong doping effect in the system. The question that remains then is which of the above effects will dominate, "the formation of potential barriers at LBGs, negatively effecting the transport properties"[9], or the efficient doping that will make the CETs a conductive channel.[1] The essence of our answer to this question is that either can dominate, depending on the preparation and the history of the Si system. In fact, even according to Ref. 9 the barriers created within the CETs are smaller than 0.1 eV, and thus, under efficient doping and the consequent narrowing of these barriers the tunneling conduction can overcome the above hinder to conduction. Noting, as in Ref. 11, that the grain boundaries in μc-Si:H are "only partially oxidized" and being aware, in view of the above, that the degree of oxidation depends on the preparation conditions further supports our explanation for the opposite results obtained by different groups.

Support for the above, within the present two studies, seems to be provided by the fact that the currents that the commenters measured were of the order of 1 pA, on both the encapsulated crystallites and the encapsulating tissue. In contrast, while we observed similar currents via the crystallites *we found orders of magnitude larger currents via the tissue* (see, e.g., Figs. 1 and 2 here, as well as ≈400 pA in Figs. 2 and 1 nA in Fig. 3, of Ref. 1). This is very large even in comparison with their "etched" (presumably "oxideless") samples. The low currents they measured, noting that their *in situ*[5,6] and *ex situ* results are similar, may support the model that they suggest for their materials since similar results were

obtained and analyzed previously in crystalline Si under various humidity conditions.[22] On the other hand, in some silicon systems the humidity appears to exhibit the opposite effect.[23] We suggest then that in our case it is the latter possibility, i.e., the doping and gettering effects, primarily by oxygen, that are responsible for the relatively high conductance that we observe. An indirect supporting evidence for that (suggesting a shallower Fermi level in our case) is that the conductivity activation energy in our samples (in the range 0.26–0.34 eV) is lower then the values (0.5 eV) reported elsewhere by the commenters.[9] We suggest then that the larger currents that we found in the encapsulating tissue reduce the possibility of space-charge or higher-resistance effects that are associated with the oxidation in the samples. We also note that the doping dominance that we suggest is not necessarily in contrast with the formation of barriers. This is since, even if the barriers exist in the CETs, the fact that the latter are heavily doped may make them thin enough to enable efficient tunneling. This is also consistent with the fact that in the high-crystallinity regime of $\mu c:Si:H$ there is a strong rise in the conductivity due to oxygen donors, in particular, for donor concentrations larger than 10^{18} cm^{-3},[7,10] as is well known to be the case also for other donors in PSi.[24] Considering the gettering effect mentioned above it is no wonder then that the columns tissue will be the preferred current route.

Our attribution of the differences in the oxygen content in the films, on the one hand, and its remarkable role on the transport properties, on the other hand, is based on the widely studied various roles of oxygen in polycrystalline silicon. Indeed, for this system it was found that there is a competition between the buildup of the oxide layers, which act as tunneling barriers, and the oxygen doping effect of the grain boundaries.[17] In fact, for PSi we noted already that the opposite effect to the one reported in the comment was found, i.e., that the HF treatment caused the reduction in the conduction, indicating that the surface area at the grain boundary was preferentially oxidized.[14] Also, in some studies it was found that "more oxynitride appears in the grain boundaries region than the intragrain region."[13] Considering the clear oxygen-doping effects in a-Si:H,[12] in polycrystalline silicon,[18] and, in particular, in μc-Si:H,[7,8] we propose then that in all these systems both the barrier build-up effect and the doping effect are active. However, the deposition and post deposition[17] conditions of the samples used determine the outcome of the "competition" between the two effects: oxygen doping being dominant in our samples while oxide barrier buildup being dominant in the work reported in the comment.

In summary, as is well known, the oxidation of Si-based systems is a complicated effect and not well understood to this date, in spite of the many relevant studies of oxide growth on grain boundaries,[13,17,18] and the "efficient" oxygen doping, as studied extensively on a-Si:H.[12] The fact that all the precautions (and more) as suggested by the commenters were applied to our samples *without changing* the current routes as well as the results of our *contactless* CITS study suggest then unequivocally that the anodic tip-oxidation effect to which the commenters soundly attribute their findings does not apply to our work. We attribute then the differences in the observations to the different oxygen contents and roles in the two types of samples.

[1] D. Azulay, I. Balberg, V. Chu, J. P. Conde, and O. Millo, Phys. Rev. B **71**, 113304 (2005).
[2] D. Will, C. Lerner, W. Fuhs, and K. Lips, Mater. Res. Soc. Symp. Proc. **467**, 361 (1997).
[3] L. Houben, M. Luysberg, P. Hapke, F. Carius, F. Finger, and H. Wagner, Philos. Mag. A **77**, 1447 (1998) and references therein.
[4] I. Balberg, Y. Dover, R. Naidis, J. P. Conde, and V. Chu, Phys. Rev. B **69**, 035203 (2004).
[5] B. Rezek, J. Stuchlik, A. Fejfar, and J. Kocka, Appl. Phys. Lett. **74**, 1475 (1999).
[6] B. Rezek, J. Stuchlik, A. Fejfar, and J. Kocka, J. Appl. Phys. **92**, 587 (2002).
[7] T. Kamei and T. Wada, J. Appl. Phys. **96**, 2087 (2004) and many references therein.
[8] W. A. Turner and G. Lucovsky, Mater. Res. Soc. Symp. Proc. **297**, 521 (1993).
[9] J. Kočka, H. Stuchlíková, M. Ledinský, J. Stuchlík, T. Mates, and A. Fejfar, Sol. Energy Mater. Sol. Cells **93**, 1444 (2009).
[10] K. Lips, P. Kanschat, D. Will, C. Lerner, and W. Fuhs, J. Non-Cryst. Solids **227-230**, 1021 (1998).
[11] S. Veprek, Z. Iqbal, R. Kuhne, P. Capezzuto, F.-A. Sarott, and J. K. Gimzewski, J. Phys. C **16**, 6241 (1983); H. Curtins and S. Vepřek, Solid State Commun. **57**, 215 (1986).
[12] See, for example, M. Aoucher, J. Mohammad-Brahim, and B. Fortin, J. Appl. Phys. **79**, 7041 (1996) and references therein.
[13] J. Lu, M. Wagener, G. Rozgonyi, J. Rand, and R. Jonczyk, J. Appl. Phys. **94**, 140 (2003).
[14] Y. Sugawara, Y. Fukano, Y. Kamihara, S. Morita, A. Nakato, T. Ida, and R. Kaneko, Ultramicroscopy **42-44**, 1372 (1992).
[15] O. Millo, D. Katz, Y.-W. Cao, and U. Banin, Phys. Rev. Lett. **86**, 5751 (2001); Y. Levi, I. Felner, U. Asaf, and O. Millo, Phys. Rev. B **60**, R15059 (1999).
[16] J.-H. Zhou, S. D. Baranovskii, S. Yamasaki, K. Ikuta, K. Tanaka, M. Kondo, A. Matsuda, and P. Thomas, Phys. Status Solidi B **205**, 147 (1998).
[17] T. Kamiya, Y. Furuta, Y. T. Tan, Z. A. K. Durrani, H. Mizuta, and H. Ahemed, Solid State Phenom. **93**, 345 (2003).
[18] B. Pivac, V. Borianovic, I. Kovacevic, and I. Zulim, Proceedings of the 28th IEEE Photovoltaic Specialists Conference, 2000 (IEEE, New York, 2000), p. 276.
[19] I. Balberg, L. F. Fonseca, S. Z. Weisz, J. P. Conde, P. Alpuinim, and V. Chu, Phys. Rev. B **63**, 113201 (2001).
[20] V. N. Mordkovich, Sov. Phys. Solid State **6**, 654 (1964).
[21] P. Torres, J. Meyer, R. Fluckiga, U. Krol, J. A. A. Seivan, H. Keppner, A. Shah, S. D. Littlewood, I. E. Kelly, and P. Giamoles, Appl. Phys. Lett. **69**, 1373 (1996).
[22] P. Avouris, T. Hertel, and R. Martel, Appl. Phys. Lett. **71**, 285 (1997).
[23] T. Kamiya, Z. A. K. Durrani, and H. Ahemed, J. Vac. Sci. Technol. B **21**, 1000 (2003).
[24] J. Y. Seto, J. Appl. Phys. **46**, 5247 (1975).