Current routes in hydrogenated microcrystalline silicon

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The numerous studies of electrical transport in undoped hydrogenated microcrystalline silicon (μc-Si:H) failed so far to establish an agreement of where does the current flow in this heterogeneous system. Here we present a comprehensive local probe investigation that solves this intriguing question and sets up a self consistent picture of the conduction mechanisms and routes in this system. The corresponding significance regarding the emerging field of percolation in semiconductor composites and the related photovoltaic applications are discussed.

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Hydrogenated microcrystalline silicon (μc-Si:H) has attracted much interest in recent years because of its promising photovoltaic properties.[1,2] The corresponding interest has drawn attention to some basic physics issues in this system; in particular, to the intriguing problems of hydrogen induced crystallization[3] and the competition between different electrical transport routes and mechanisms in it.[4–7] The latter problem, with which we are concerned here, is of general physics interest as it touches upon the intricate percolation problem in semiconductor composites, whose study is still at its infancy. The complexity of the latter problem, in comparison with classical percolation theory,[8] involves three factors. First, at least two phases, as well as the interface regions between them, may be involved in the transport. Second, charge transfer between elements of the same phase may be nontrivial involving tunneling or thermal emission, and third, there may be a connected network of aggregates of such elements. The main problem regarding such composites is then the determination of the dominant electrical conducting network and the related transport mechanism. As will be described below, μc-Si:H is a prototype of such a composite. By macroscopic measurements one can determine the dominant transport mechanism in such a system, as we have done in Ref. 7, but not the specific network responsible for the observed electrical conduction. In order to get a comprehensive picture of the percolation conduction in such a system we report in this paper on "where" the current flows noting that we have resolved the corresponding "how" question in Ref. 7. Correspondingly, in the present study not only did we reveal the dominant conducting networks as a function of the crystallite silicon content, x, but we also put the many fragments of macroscopic data on the transport in this system into one framework. Our above approach seems to be helpful in the study of other semiconductor composites and in particular in polycrystalline semiconductors. This is not only within the academic interest, as described above, but also for applications such as photovoltaic devices. In the latter context we note that the route and mechanism we found in the present study (conduction in the disordered tissue that encapsulates the crystallites columns, see below) and in Ref. 7 (conduction in a disordered tissue with carrier-type inversion there) are vary reminiscent of the phenomena found recently[9] in polycrystalline CdTe, that was suggested to be associated with its improved photovoltaic properties. In fact a similar role of the conducting networks has been recognized[10,11] in various polycrystalline systems.

μc-Si:H is actually a wide class of heterogeneous materials[5,7] consisting of a microcrystallites phase with volume fraction x, an amorphous (a-Si:H) phase and, in some cases, voids.[4,12–15] In between elements of each pair of phases there is a corresponding disordered silicon tissue, or boundary.[4,5,7,16] In addition, there is a disordered silicon tissue that may form a barrier between adjacent ("touching") individual crystallites,[4,17] and another tissue that encapsulates the crystallites aggregates that have the form of columns in the direction of the film growth.[5,7,12,13] In particular, it has been systematically shown[12] that the latter structure is well developed in samples *with x larger than 0.5,* such as the systems that exhibited the improved photovoltaic properties (usually for $x \approx 0.7 \pm 0.1$).[2,18,19]

Numerous papers have been published on macroscopic transport measurements in the latter systems and essentially all possible current flow scenarios that follow from the above heterogeneous structure have been proposed.[4,5,20,21] Such are the intercrystallite transport models,[17,22,23] the a-Si:H phase model,[4,24,25] and various disordered tissues models.[4,5,7,26] In the high-x regime, two additional possible scenarios, illustrated in Fig. 1(a), have been considered: transport via the crystallites columns[4,13,15,16] and transport in the disordered tissue[13,19] that encapsulates them.

An obvious conclusion from the above collection of interpretations, based on macroscopic measurements, is that these cannot distinguish reliably between the various current-flow scenarios and that a direct experimental determination is called for. This was realized by Rezek *et al.*[27] who applied conductive atomic force microscopy (C-AFM) to high-x undoped μc-Si:H, and by Ross *et al.*[28] who used scanning tunneling microscopy (STM) to low-x doped μc-Si:H samples. The latter study has shown that conduction takes place through the individual crystallites, consistent with macroscopic data and in accord with the relatively high conductivity of those crystallites.[17,22,23,25] The fact that the same

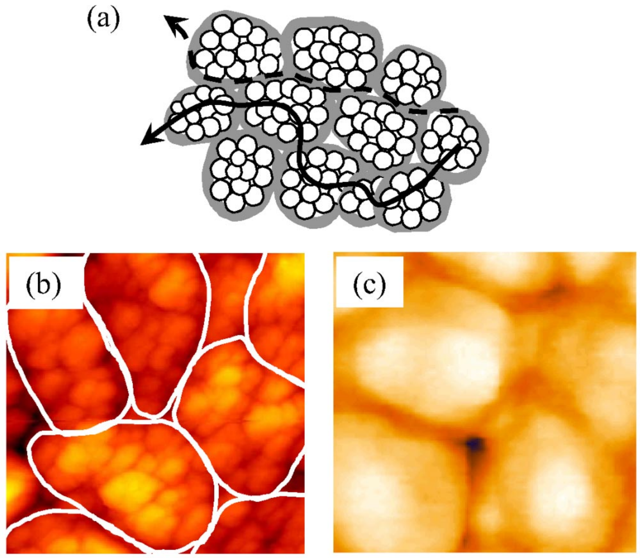

FIG. 1. (Color online) (a) Schematic top view of the μc-Si:H film showing the columns' tops and the surrounding disordered Si tissue (gray). Two possible conduction paths are shown, through the crystallites (solid line), and through the disordered Si tissue (dashed line). (b) STM image of a μc-Si:H sample prepared by HW-CVD. The white curves mark the crystallites columns edges. STM settings: $V=1.5$ V, $I=0.1$ nA. (c) AFM phase-imaging map portraying the μc-Si:H columns (brighter regions) that are surrounded by a disordered Si tissue. Color/gray scale ranges: 23 nm in the topography image and 8° in the phase image. Both images are 0.2 $\times 0.2$ μm^2 in size.

conclusion was drawn from the C-AFM experiments,[27] however, did not yield a consistent picture since for such systems *the macroscopic data of many groups*,[4,15,25,26] *including ours*[7] *and those of the group that performed the C-AFM measurements*,[5,6] suggested that transport takes place in some disordered silicon tissue, rather than via the crystallites. Following this discrepancy and searching for a self consistent picture of the current networks in μc-Si:H we turned to a comprehensive scanning probe microscopy study on the *very same* undoped μc-Si:H, samples on which we have previously determined the transport mechanism.[7]

Our μc-Si:H films, about 1 μm thick, were grown by the hot-wire chemical vapor deposition (HW-CVD) technique or the radio frequency plasma-enhanced chemical vapor deposition (rf-PECVD) technique. The details of the deposition process and a full report on their structural and optical properties as well as on their electrical conductivity can be found in Refs. 29 and 30. The silicon crystallite content was controlled by the degree of hydrogen dilution and characterized by Raman spectroscopy.[12,29,30] Samples for "lateral transport" measurements were deposited on a Corning glass substrate, and a gold strip evaporated onto one edge served as a counter electrode to the conductive AFM tip that scanned a few millimeters away from it. For the "vertical transport" configuration the samples were deposited onto Au/Cr films predeposited on a glass substrate, that served as a counter electrode. The C-AFM data were acquired in the constant force mode, using various types of conductive tips.[31]

For the single phase $(x\approx 1)$ μc-Si:H we also performed STM measurements, in particular current imaging tunneling spectroscopy (CITS). In this mode[32] the topographic map is derived as usual, but at each point the feedback is disconnected momentarily and the tunneling current is acquired for a bias that is different than the one used in the topographic map.

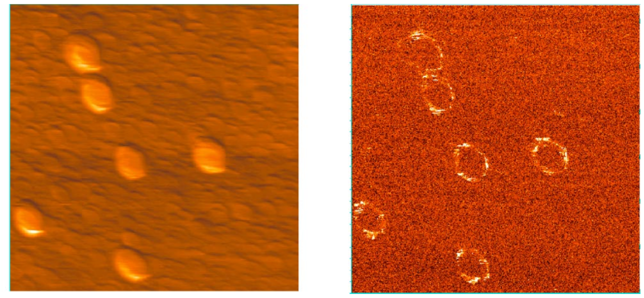

FIG. 2. (Color online) C-AFM images $(2.5\times 2.5\ \mu m^2)$ acquired in the vertical-transport configuration on a sample that contains mostly *a*-Si:H. The current image (to the right) was acquired at a bias voltage of 10 V. Color/gray scale ranges: 45 nm in the topographic image and 0.4 nA in the current image.

Turning to our experimental results, we show in Fig. 1(b) a STM topographic image of single-phase μc-Si:H. Here we see that the crystallites' aggregates (encircled by curves) are composed of microcrystallites with diameters of about 20 nm, in good agreement with the values we estimated from our Raman spectra.[29,30] The STM image, however, does not yield any contrast between the crystallites and the (possibly existing[10]) disordered Si tissues. Such information, which obviously is of utmost importance for the present investigation, is provided by monitoring the phase shift in AFM tapping mode measurements, known to yield material-dependent contrast.[33] Figure 1(c) shows a phase-shift map of an $x\approx 1$ sample. While not resolving the inner crystallite structure of the columns, it is evident that they are encapsulated by a different material, which can be attributed to a disordered Si tissue that forms a continuous geometrical, and thus a possible conducting, percolation network.

Considering the current flow, we examined whether the column tissue has a higher conductivity in comparison with the crystallite aggregates within the columns themselves and/or the *a*-Si:H matrix. This was done by using a thin film (0.3 μm thick) in the vertical transport configuration with an $x\approx 0.2$, low enough, to avoid lateral conduction between the columns but high enough to have some columns. The C-AFM data shown in Fig. 2 demonstrate that indeed the current flows in the columnar-disordered tissue, as the "rings" in the current image and the columns diameter [see also Fig. 1(b)] are both about 0.1 μm. Thus, the conductivity of the column's tissue is seen to dominate over the other possible routes.

For the high-x contents we examined films, with $x\approx 1$, in both the "vertical" and "lateral" configurations. Results obtained in the lateral transport configuration, which were qualitatively the same as those measured in the vertical configuration, are exhibited in Fig. 3. They show that the current flows mainly at the column boundaries, namely, *through a disordered Si tissue, and not through the crystallites*. This is

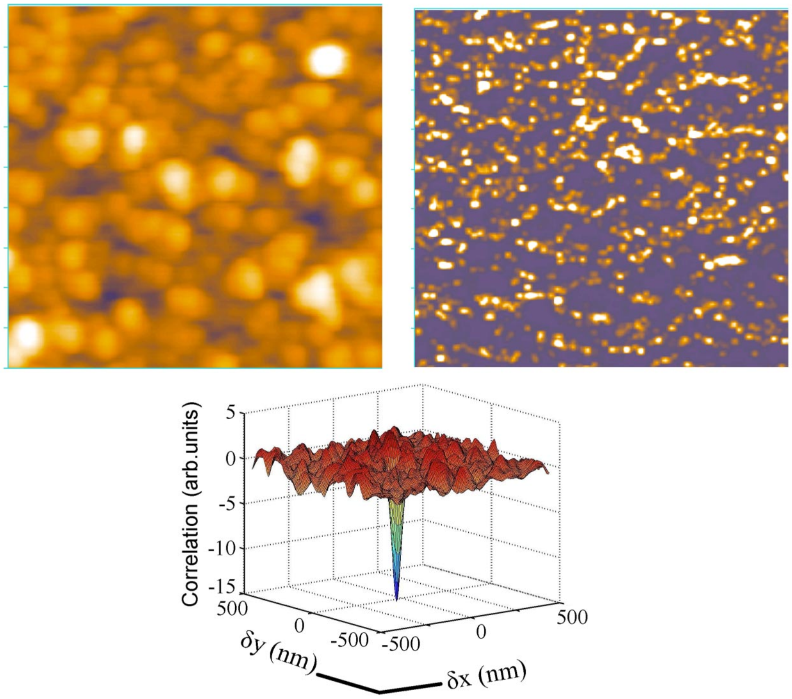

FIG. 3. (Color online) $1\times1\ \mu\mathrm{m}^2$ AFM topography image (left panel) and lateral-transport current map at $V=6$ V (right panel) acquired simultaneously on a μc-Si:H film (prepared by HW-CVD). The disordered tissue that encapsulates the crystallites columns forms a continuous percolation network and the current flows mainly through that network. Color/gray scale ranges are: 30 nm in the topography image and 1 nA in the current image. The inset shows the cross-correlation function of the two images.

clearly portrayed also by the normalized topography-current cross-correlation function plotted in the inset. At zero relative displacement (graph center) the cross-correlation function attains a minimal (negative) value, reflecting the fact that maximal local current is obtained at the columns-interface (deeper) regions. However, now, from the examination of the lateral configuration, it is also clear that the "touching" columnar tissues form a lateral percolating network.

Since our above findings are in contrast with the C-AFM results reported by Rezek *et al.*,[27] we carried out many tests that have shown that no artifacts associated with tip-sample contact are involved. In particular, to get a completely independent test of our conclusions we have also performed *contact-less* STM-CITS measurements, the results of which are displayed in Fig. 4. Here, again, the current flows primarily at the boundaries of the crystallite columns, in particular it exceeds the current through the boundaries of the individual crystallites. These CITS measurements thus corroborate our C-AFM results, and in particular conclusively exclude the possibility that the latter were dominated by any tip-sample contact effect. We note that the results were always qualitatively the same for both HW-CVD and rf-PECVD films, thus establishing the generality of our results for μc-Si:H systems.

The discrepancy between the macroscopic and microscopic results of Rezek *et al.*[27] and the corresponding self consistency in our experiments can be explained as follows. They found a dominant tissuelike conduction in their macroscopic measurements,[5] for "regularly" deposited samples, but a conduction that appeared to take place through the crystallites in their microscopic measurements,[27] on samples deposited at ultrahigh vacuum. Following the previously suggested[34,35] efficient and strong oxygen doping effect of, apparently, the column's encapsulating tissue, it is very likely that in the regularly deposited samples the dominant transport is via this oxygen unintentionally doped tissue while the opposite applies to the films prepared under ultrahigh vacuum conditions.

In order to find the relation between the many studies that suggested[4,5,7,13,21] transport in a disordered tissue and the above derived dominant transport route, we have also carried out C-AFM measurements in the lateral configuration on a mixed phase μc-Si:H/a-Si:H system with $x\approx0.5$. The corresponding results indicated that the current *does not* flow through the columns' tissue network, but rather through the a-Si:H matrix, although its conductivity is much smaller in comparison with the one observed in the columns' tissue of the $x\approx1.0$ samples. This is well understood now to be due to the fact that no lateral percolation network of the columnar disordered tissue is completed here. It is thus also apparent

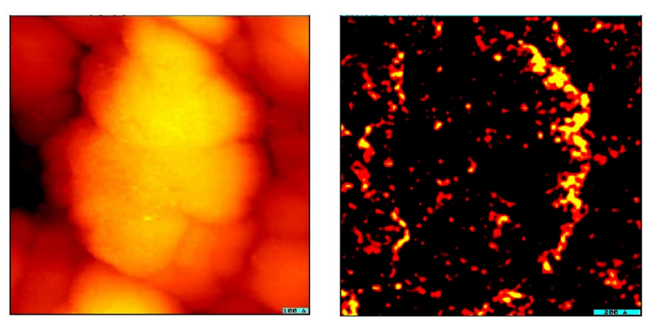

FIG. 4. (Color online) CITS images ($0.12\times0.12\ \mu\mathrm{m}^2$), focusing on a single column, obtained on a single-phase μc-Si:H film. The topography image (setting: $V=2$ V, $I=0.1$ nA) is shown to the left and the current image (at 3.5 V) to the right, portraying enhanced current in the encapsulating disordered tissue. Color/gray scale ranges: 15 nm in the topography image and 0.4–7.4 nA in the current image.

that the large "jump" observed[5] in the macroscopic lateral conductivity for $x \approx 0.7$ is associated with the formation of that connected network.

Our present results enable now the understanding of the sharp percolation transition at low x (~ 0.3) values that was reported for n-type[17,21,23] and p-type[26] doped materials, and the relatively high-x (~ 0.7) percolation threshold that we[29,30] and others[4,5] found in undoped systems. According to the structural data[12] and the present detection of the conducting columnar tissue, one would expect *two subsequent percolation transitions in μc-Si:H*; a low-x transition that is associated with conduction in a regular percolation system made of sphericallike conducting particles,[36] and another, high-x transition, that is associated with the intercolumn tissue, such as the one observed in a network of conducting sheets.[37] While the low-x value is well understood[21,36] the high-x value is not, since the relation between the tissue content and x is not a straight forward matter.[20] However, following the two dimensional Scher and Zallen prediction[36] and considering straight cylindrical columns, one would expect that the high-x value will be 0.45. Adding to that the crystallites that are outside the columns, a corresponding percolation transition in the $0.7 \geqslant x \geqslant 0.5$ range is to be expected. In fact a close examination of the data of us[29,30] and others[5,19] confirms these expectations. In particular, one can see that the data of Koynov *et al.*[15] exhibit very clearly the existence of the presently predicted two subsequent percolation transitions scenario. They found in undoped μc-Si:H a conductivity transition from 10^{-12} to 10^{-9} $(\Omega\,\mathrm{cm})^{-1}$ at a low-x value, and a subsequent conductivity transition between 10^{-8} and 10^{-3} $(\Omega\,\mathrm{cm})^{-1}$ at a higher-x value. We were able to repeat their findings, on our films, with our deposition technique indicating their generality for the μc-Si:H system. We were able to repeat their findings, on our films, that were prepared under somewhat different conditions, indicating the generality of these two percolation transitions in the μc-Si:H system. Considering the tunneling or thermal emission conduction suggested[17,22,23] for the low-x regime and the band-tails conduction that we and others suggested[5,7] for the high-x regime, we obtain now *a comprehensive picture of the electronic transport in μc-Si:H*. This picture enables us now to review the many data in the literature within the framework of two types of percolation networks. Moreover, the optimized crystalline content of $x \approx 0.7$, for solar cell operation,[2,5,18] is suggested now to be associated with the onset of connectivity of the columns tissues network.

In summary, our comprehensive local probe study clearly indicates that the dominant transport route in undoped μc-Si:H is in the disordered tissue that encapsulates the crystallites columns. This conclusion seems to explain the fundamentals of the transport phenomena observed in this system and provides a general approach for the evaluation of electrical transport in other semiconductor composites.

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