Growth Mechanisms and Characterization of Hydrogenated Amorphous-Silicon-Alloy Films

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A. Gallagher, D. Tanenbaum,
A. Laracuente, E. Molenbroek
*National Institute of Standards and
Technology
Boulder, Colorado*

NREL technical monitor: W. Luft

National Renewable Energy Laboratory
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SUMMARY

Goal:

The overall objective of this work is to better understand the atomic-scale structure of glow-discharge-produced a-Si:H, a-Ge:H, and a-Si:Ge:H films, its effect on film quality, and its dependence on deposition discharge conditions. A secondary objective is to establish a definitive, in-situ diagnostic of film quality that could be used to efficiently optimize process parameters in photovoltaic production systems. The approach taken is to measure the morphology and chemical characteristics of the as-grown film surface with atomic-scale resolution using a scanning tunneling microscope (STM). Many of the limitations of a-Si:H-based photovoltaics are attributed to microvoids, boundary defects, and microparticulate incorporation, and all of these should be visible at the surface of the growing film using STM.

Results:

We have measured the surface shape of intrinsic a-Si:H films with atomic resolution, as a function of film thickness. The films were deposited at $T_s = 30^\circ\text{C}$ and 250°C from a silane rf glow discharge using device-quality deposition conditions of 0.5 Torr silane pressure, 1.7 Å/s deposition rate and small power/flow; IR absorption, σ_L and σ_D indicate high quality films. The films initially conform smoothly to an atomically flat Si or GaAs substrate, but as the thickness increases the roughness steadily increases to approximately 10% of the length of the scanned region. The surface of 100-400 nm thick films is highly inhomogeneous, with steep hills and canyons in some areas and large atomically smooth regions in others. These unexpectedly large surface irregularities indicate severe and often connected void structures in the growing film, as well as relatively limited-range surface diffusion of the incorporating SiH_3 radicals.

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Introduction

The gas-phase plasma chemistry leading to glow-discharge a-Si:H film deposition has been studied rather thoroughly, and the primary mechanisms and species responsible for film growth are now fairly well understood.¹⁻⁴ Similarly, the electrical and related properties of this semiconducting film have been extensively diagnosed, and many characteristics are now fairly well understood.⁵⁻⁷ In contrast there have been very few studies, and only vague models, of the growing film surface where the structural and electrical properties of the film are produced. Ellipsometry measurements^{8,9} have investigated early-growth irregularities, and we have shown that the growing film has a very thin (1-2 atomic layers) hydrogen-rich surface.¹⁰ However, such measurements detect surface averages, whereas structural irregularities are believed to be responsible for many key properties and limitations of a-Si:H photovoltaics.¹¹ Consequently, we are studying here the atomic morphology, and if possible the individual species, at the growing film surface using a scanning tunneling microscope (STM). Kazmerski¹² and Wiesendanger et al.¹³ have obtained STM measurements of a-Si:H film surfaces, showing that atomic-scale species and morphology information can indeed be achieved on the surface of these amorphous materials. Our program is designed to carry this capability toward much more extensive measurements of many surface regions -- to alloys and to surfaces deposited under a variety of deposition parameters. It is commonly believed, from bulk-film measurements, that the critical electrical properties of these films are largely determined by their inhomogeneities, including those that occur rather infrequently.^{11,14-16} Thus, extensive studies of many surface regions and deposition conditions appear necessary to elucidate the causes of the film structural features that limit photovoltaic efficiency and stability.

Technical Approach

We expect the initial atomic-scale morphology of C, Si, Ge, and H deposition from a glow discharge into a-Si:H and alloy films to depend strongly on the atomic-scale roughness and chemical composition of the substrate. To minimize the effect of such uncontrolled roughness and to optimize the connection to a large body of surface-science knowledge, we are currently studying a-Si:H and alloy-film deposition onto oriented, atomically smooth, and clean surfaces of crystal Si and GaAs, prepared in ultra-high-vacuum (UHV).

As shown in Fig. 1, the film deposition is done in an attached, turbomolecular pumped chamber, and film-coated substrates are transferred through a gate valve into the UHV chamber after termination of the glow discharge and deposition-gas flows. This pump down, sample cooling, and sample transfer into the STM typically requires ~30 minutes, during which time the sample is exposed briefly to $\sim 10^{-8}$ Torr and, thereafter, to $< 10^{-10}$ Torr of impurities (primarily H_2 , SiH_4 , CO , and CO_2) in the two chambers. This represents ~8 molecules per surface atom impinging on the surface before observation; this is not expected

Fig. 1 Schematic of the film-deposition and diagnosis apparatus. The UHV chamber, left, is ion and Ti-sublimation pumped while the film-deposition chamber, right, is turbo-molecular pumped. The substrate holder is moved after deposition as indicated by the arrow, so that the transfer rod can remove and transfer the substrate to the UHV manipulator.

to significantly alter the exceptionally inert a-Si:H surface. (This is $\sim 10^{-8}$ of a one-minute exposure to the reactants in air.) We have measured the effect of air exposures of 1-100 minutes; we observe a gradual increase in surface carbon and in surface resistance to tunneling. This indicates that we can carry out valid studies of samples prepared in other laboratories and transferred to an evacuated container for shipment. It also shows that residual gas exposure inside our vacuum system has a negligible effect. Repeated and varied depositions on a single sample can be studied in this experimental arrangement without exposure to air. However, we do not yet have the ability to refind a particular location or feature after the film has been transferred back and forth between the deposition and UHV chambers. In essence, the STM scans arbitrary regions of $\sim 0.5 \mu\text{m} \times 0.5 \mu\text{m}$, and our sample positioning is not sufficiently accurate to refind such a small area. A new STM has been under construction and development for the past year, and it includes such capability but is not yet in operation.

Our film-deposition region is designed and operated to mimic conditions and arrangements most commonly used to produce device-quality a-Si:H and alloy films by glow-discharge deposition. However, the special requirement of sample transfer into the STM necessitates some unusual arrangements, as seen in a detail of the deposition region shown in Fig. 2. As shown there, the sample is mounted on a holder that is transferred between the discharge region and the STM. This holder also contains separate connections to two sides of the crystal to allow resistive heating during sample preparation. Also, the substrate surface is slightly above the plane of the grounded electrode, with some slightly recessed and protruding regions nearby. When film is deposited, the entire discharge region, shower head, and sample are heated to the substrate temperature. The rf electrode is 5-cm square and 2 cm from the substrate electrode, defining the discharge volume and yielding a relatively uniform discharge region at the sample. Deposition rate is measured with laser interference fringes and is normally 1-2 Å/s.

Tunneling Conditions

Due to the large scale of film surface roughness compared to the STM tunneling gap of 5-10 Å, we always scanned the surface in the constant-current tunneling mode. However, we frequently interspersed this with current (i) versus probe-height (z) data at a point with constant voltage (V). If the probe penetrates the sample, as occurs with insufficient voltage or excessive current, this produces a very gradual and often irregular decrease in i with increasing z . If excessive voltage is applied at constant current, this induces irregular z fluctuations versus time at a point due to atomic and bonding rearrangements. If the tungsten probe is "dirty," or covered with nonmetallic atomic layers such as oxide or Si, then $i(z)$ again falls relatively gradually as z is increased. When the probe was clean and current and voltage conditions were optimized, we observed stable $z(t)$ at constant i , and $i(z) \propto \exp(z/z_0)$, where the scale height z_0 is < 2 Å. This rapid current variation with z indicated the desired tunneling through a small vacuum gap between sample and probe, and that the topography obtained from a constant-current scan closely represents the actual surface shape.

Fig. 2 Details of the glow-discharge film-deposition region. All materials are stainless steel, except as noted, plus the alumina rf-feedthrough insulator and a molybdenum substrate holder.

Different surface states at different sample positions can still produce apparent height variations, but these are expected to be small ($< 2 \text{ \AA}$) under these circumstances. All data presented below were obtained under conditions that produced $z_0 < 1.5 \text{ \AA}$ and "quiet" $i(t)$.

From the standpoint of STM tunneling theory, it is interesting that the sample voltage necessary to obtain equivalent vacuum tunneling (based on exponential $i(z)$ into $4000 \text{ \AA}$ thick films) varied between -1.5 and -6 V at different times (with the probe effectively grounded). This large variation is clearly related to atomic-scale changes in the shape of the probe and its coverage by a-Si:H debris. In a variety of instances we scanned surface regions at very different sample voltages, confirming that the detected topography was normally independent of the voltage. However, severe height fluctuations related to probe instabilities sometimes occurred outside a narrow voltage range.

Current-voltage (I - V) curves obtained with z fixed at any point on the $4000 \text{ \AA}$ intrinsic film were asymmetric. As seen in Fig. 3, the positive sample voltage required to generate a given current is several volts larger than the negative voltage necessary to achieve the equivalent current. This behavior occurred for 0.02 to 3 nA tunneling current, and was *independent of the sign of the Si substrate doping*. Qualitatively similar n-type Schottky-diode behavior is shown in Fig. 3 from chromium dots evaporated on the exposed surface of the same a-Si:H film, with ohmic contact to the backside of the crystalline substrate made by diffusing indium into the silicon. This simulates the operation of the STM, with the chromium dots effectively replacing the STM probe. An equivalent current density was obtained if one assigned an effective area of $\sim (800 \text{ \AA})^2$ to the STM current. A reasonable interpretation of the forward-bias STM current is thermionic electron emission over the low barrier in the a-Si:H, accompanied by tunneling through the high, thin vacuum barrier. The increased a-Si:H barrier under reverse bias then limits the reverse current, yielding Schottky-diode-like STM behavior. Similar asymmetric behavior has been reported for tunneling into crystal Si (Ref. 17) and H terminated Si (Ref. 18) with opposite dependencies on doping.

In order to further verify that the observed surface topography of this highly resistive film was a valid representation of the surface, we scanned some areas of the $4000 \text{ \AA}$ thick films at several sample voltages (3 - 6 V) and with varying illuminations with a 633 nm laser beam. (The beam intensity inside the film was estimated at $\sim 10 \text{ mW/cm}^2$. This intensity normally lowers the low-field resistivity from $> 10^9$ to $< 10^5 \text{ \Omega cm}$.) Essentially identical topographies were obtained at the different voltages, and in most instances with different illuminations as well. Switching on the illumination normally caused the STM probe to back away by 1 - $4 \text{ \AA}$, but occasionally by as much as $20 \text{ \AA}$ at some locations. We suspect this is due to varying probe and film surface states, some of whose occupancy may be light sensitive. It is important to note that this can be taken as a worst case limit of local electronic effects on our topographic data, and cannot represent the much larger roughness we measure. Data reported here were obtained under circumstances where the illumination had a relatively minor effect on the tunneling gap, and did not significantly alter the observed topography.

Fig. 3 Two examples of current voltage spectroscopy on 4000 Å a-SiH films deposited on crystal silicon. The left axis scales the STM data, while the right side scales data for a 0.02 cm² chromium spot evaporated on the film surface.

Resolution

The recorded topography represents a nonlinear convolution of the probe surface with the sample surface, at a fixed spacing of typically ~ 5 Å. This is less important in studies of essentially atomically flat crystal surfaces, as the surface height varies by only a few Å. However, it is crucial when looking for nm size irregularities and incipient voids on the surface of a-Si:H films. Examples of this contact transform are shown in Fig. 4, for an idealized probe shape. Note that sample protrusions appear broadened, but with true height, while sample valleys appear with decreased width and sometimes decreased depth. (As can be seen in the figure, only the ratios of probe diameter to feature dimensions are relevant. However, it appears that our probe ends typically had a radius of ~ 20 Å.) More detailed analysis of image distortions by probe shapes have been reported.^{19,20} We have considered these effects in our data analysis, and some examples will be given below. If the narrowest, steepest hills recorded by the STM were the result of a delta-function type feature on the surface, these hills would be upside down (inverted) images of the probe, ignoring the 5-10 Å tunneling gap. If the tunneling gap and a width of the surface feature are included, the probe must be even narrower. Using this fact, we use cross sections through the steepest, narrowest hills observed in a given set of scans to define an upper limit to the probe resolution. This cross section can then be inverted and considered as the outer limit to the probe plus tunneling-gap shape, as seen in Fig. 4(b). This inverted cross section (ICS) can then be compared to any features on other scans. If the ICS is much narrower than any feature in a scan, then the scan topography closely resembles the actual topography. If desired, one can estimate that hills will appear broadened by $\sim 50\%$ of the ICS width, and valleys will appear narrowed by the same amount. The end of most probes, as seen in the ICS obtained here, are relatively blunt on a nm scale. To see how this influences images of surface valleys or pits, we have shown in Fig. 4(a) two probe sizes transformed with one valley and the resulting scan lines. Note that the scan line has a flat bottom if the probe fits in, whereas it has a cusp-shaped bottom if the probe is too wide. We use this fact to look for steep-sided, narrow holes and valleys; examples will be given below.

Morphology of a-Si:H Film Surfaces

Topography data are presented for 100, 600, 1000 and 4000 Å thick films, all deposited at 250°C substrate temperature and ~ 1.7 Å/s deposition rate. In each case data were taken from ~ 30 minutes to a week after deposition, and no indications of systematic changes were found over this time interval in the UHV chamber. However, apparent fine-scale topography changes did sometimes result from varying tunneling voltage, from probe-tip cleaning by voltage pulsing, by illuminating the film (~ 30 mW/cm²), and occasionally during repeated scans without any deliberate changes in conditions. In addition, many scans exhibited scan-direction streaks and height steps (usually 1-10 Å), due to temporary offsets in the tunneling gap. (These are easily distinguished from actual topography by their direction and their occurrence in single scan lines.) These height steps are attributed to changes in the atomic arrangements and surface states on the probe. The a-Si:H film is not very robust, compared to crystal Si or metals, and it appears that film components are very easily transferred to the probe during approach and scanning. We suspect that this debris is loosely bonded to the W

Fig. 4 Examples of the STM scan lines produced by various probe and sample shapes

probe, and is easily shifted around by the strong fields and high current densities (electrophoresis) at the tunneling point. The data presented here are selected from periods when more stable and reproducible scans were obtained. Surface topographies inferred from the noisy periods are consistent with these data, and it appears that the topographies reported here are indicative of the entire surface.

A. 100 Å thick film

Two surface regions of a 100 Å thick film, deposited onto vacuum-cleaved GaAs (110), are shown in Fig. 5. These surface regions are flat within two atomic layers with rms height variations of ~ 2 Å, and are typical of those observed. Many of the (typically ~ 3 Å high and 40 Å wide) lumps in Fig. 5 did not reproduce well in repeated scans, and one can see streaks and "shelves" of ~ 1 Å height in the x direction in both scans. These indicate residual probe-tip instabilities, and they suggest that one should not overly interpret features < 3 Å high in Fig. 5. Some 10-20 Å high hills of ~ 50 Å width were very occasionally observed on this surface. It is not clear if these were discharged-produced microparticulates deposited during film growth or at the termination of the discharge, particulates released from other surfaces during sample transfer, or simply growth structures. In either event, they provided a useful diagnostic of probe resolution; from their shape we estimate an upper limit on the probe tip radius. In Fig. 5(b) a contour through one such nearly-cylindrical hill is shown inverted; the actual probe resolution, including the vacuum gap, must be sharper than this. This is compared in Fig. 5(b) to the line shown through the tallest and deepest features in the part (a) image, which was obtained in the next scan. The inverted hill is narrower than any features in this line, and we conclude that the topographies in parts (a) and (b) correctly represent most aspects of the film surface. However, the hill has a rounded tip on a 10 Å scale, and surface pits of this size or smaller probably would have escaped detection.

Overall, the measured 100 Å film surface topographies appear very flat, typically having two atomic layers (5 Å) of height variations in the form of 30-100 Å wide lumps. There are no indications that islands formed during the initial growth. 100 Å films were also deposited on n type Si (111) surfaces, prepared by Shiraki etching and thermal oxide removal in vacuum. Surface topographies on these films were generally consistent with Fig. 5, but less conclusive since some regions of the initial crystal surfaces were not atomically flat and clean. Since this initial perfect atomic flatness was not deemed necessary for thicker films, those films were deposited on crystal silicon to more closely mimic the standard film growth geometry used in photovoltaics.

B. 600 Å thick film

The surfaces of 600 Å thick films were much rougher and more varied than for the above 100 Å thick films. A variety of differently shaped landscapes were observed, but will not be shown here as similar examples are shown below for 1000 Å and 4000 Å thick films.

Fig. 5. STM scans of two surface regions of $100 \text{ \AA}$ thick intrinsic a-Si:H films, deposited onto a GaAs crystal. The scan line in (a) is reproduced in (b) together with a probe-resolution line.

Fig. 6 STM image of a 60 nm thick intrinsic a-Si-H film deposited on crystal Si

Figure 6 gives one rather severe example from the 600 Å thick film, which demonstrates long connected valleys.

C. 1000 Å and 4000 Å thick films

Surface topographies on 1000 Å thick films deposited on p-type, 20 Ω cm, (100) Si and 4000 Å thick films, deposited on n type, ~0.01 Ω cm, Si (111) substrates will be shown. These often have a rougher character than seen on the 600 Å thick film, while the topography of the 1000 Å film is generally similar to that of the 4000 Å film. The surface-height range seen in the 600 Å thick film have increased at 1000 Å of film growth, but the surface appears to have then reached a relatively stable form during further growth. We have observed many kinds of surface topographies and features in the thicker films, and we will discuss and provide a variety of examples of these. The total height range, ΔZ , observed on each scan depends on the lateral scan size, ΔX , and varied considerably between different regions. In Fig. 7 we show the full range of ΔZ , versus ΔX , observed on 100, 600, 1000, and 4000 Å thick films.

"Hilly" areas, consisting of apparently randomly placed, rounded hills covering the entire scanned region are found most often. Three examples are given in Fig. 8. The individual hills have rather low surface slopes, generally <0.2 from horizontal, and their lateral sizes vary from 50-2000 Å. The valleys between hills are generally broad and flat. As can be seen in Fig. 8, the typical size of these hills can vary greatly between different scanned regions, even on the same film; hills of successively larger size are shown parts (a)-(c). Note that each edge of each figure provides a *de facto* scan line through the figure, but with slopes exaggerated 3 times since the vertical scales have been 3 times expanded. Based on detecting occasional hills that are steeper and smaller than any features in Fig. 8, in other regions scanned before or after these areas (one of these is shown in Fig. 9), we believe that the topographies in Fig. 8 closely represent the large-scale surface shapes, without smearing by the probe resolution. Since height data were recorded at 10 Å steps in these scans, and the small hills such as those in Fig. 9 have 10-20 Å wide rounded tops, "large-scale" here means >20 Å.

A small, steep hill is shown in lines a-b and c-d of Fig. 9, which is a higher resolution scan (2 Å between data points) of a region nearby that in Fig. 8(b). The region in Fig. 9 may also be characterized as "hilly" on a finer scale than in Fig. 8(a), but these smaller hills are not just a smaller version of the hills in Fig. 8(a). The latter are relatively smooth with low slopes and broad valleys between, whereas the small hills in Fig. 9 have steep sides and often narrow valleys. In fact, the data in Fig. 9 are undoubtedly smeared by probe resolution and the actual surface bumps are sharper than they appear. We will return to this figure below, in the context of incipient voids.

In complete contrast to the hilly areas described above, some surface regions are extremely smooth. Several examples are given in Figs. 10 and 11. The steepest slope across large

Fig. 7 The full height range Δz (after deplaning) of various scanned surface regions, versus the size $\Delta x = \Delta y$ of the scanned region, for 100 Å, 1000 Å, and 4000 Å thick films.

Fig. 8 Three examples of hilly surface regions, with varying hill size. (a) and (c) are from a $4000 \text{ \AA}$ thick films, and (b) is from a $1000 \text{ \AA}$ thick film. Data points were taken at $10 \text{ \AA}$ intervals.

Fig. 9 A region of small, steep hills from a 1000 Å thick film. Data points are at 2 Å intervals. Part (b) shows cross section lines through locations shown in (a). The probable probe shape is indicated under line a-b. Shaded regions indicate where the actual a-Si:H surface could be below the scan line, due to the probe effect shown in line B of Fig. 2(a). The arrow in line e-f identifies a region that is similar to line A in Fig. 2(a). The dashed lines on either side of the arrow indicate the probable a-Si:H surface.

Fig. 10

An example of a smooth region, of a 4000 Å thick film. Data were recorded at 15 Å intervals.

regions of the surface in Fig. 10 is only 0.04, and local regions of the surface appear to be extremely smooth. This overall smoothness is partly obscured by a probe-tip instability that caused 5-10 Å height fluctuations, but as these occur at random positions and generally form single scan-line, streaks; they can be readily distinguished from the actual surface. In fact, this instability is so clear in this figure precisely because the actual surface is exceedingly smooth, generally with less than 5 Å height variations across 500 Å wide regions.

Figure 11 shows another flat region, as well as an exceptional view of the inhomogeneous character of the film surface. The left front quadrant of the 1000 Å square region in Fig. 11(a) is hilly, with close-packed hills of ~ 40 Å height and 100 Å width, having side slopes of ~ 0.3 . The remaining three quadrants are flat within 5 Å, and as seen in Fig. 11(b) a 100 Å square region at the front corner is flat within 2 Å. This degree of flatness on a 4000 Å thick film is very impressive. It is important to note that because steep hills were observed in the same (part (a)) scan that showed the flat region, the flat portions of the image cannot be an artifact created by low probe resolution.

D. Voids

As noted in the introduction, many voids are believed to occur in a-Si:H films and to be important contributors to the electronic properties.^{10,11} In order to discern such voids in the act of forming at the surface, we have searched our data for relevant features. As discussed in the "resolution" section, all such low regions will be observed with an STM as narrower and often shallower than the actual shape. As shown in Fig. 4(a), the contact transform, at ~ 5 Å gap, of the inverted probe tip with a pit of comparable or smaller width will produce a cusp-shaped scan pit with a sharp point at the bottom. We have so far found two forms of such incipient voids; one form is a long canyon and the other is at low points between hills. An example of the former is given in Fig. 12, while Fig. 9 provides examples of the latter. Figure 12(a) shows a canyon, with observed depth of ~ 20 Å. The cross-section line in Fig. 12(b) shows the cusp-like shape expected when the probe-tip diameter exceeds the canyon width; the canyon bottom is not reached in this case. The sides of these cusps are steeply sloped ($> 45^\circ$), further supporting the implication that these are incipient voids.

Figure 9(b) shows cross-section contours through a variety of the small hills in Fig. 9(a). These contours contain many cusp-shaped pits at the contacts between hills.

Discussion

Intrinsic a-Si:H films, deposited by silane glow discharge, are known to be amorphous and comprised mainly of 4-fold coordinated Si atoms with bond lengths and angles very close to crystalline values. However, the density is typically 5% below the crystalline density and typically contains $\sim 10\%$ hydrogen atoms. The simplest way to reconcile these apparent

Fig. 11 A surface region of a 4000 Å thick film, scanned at 10 Å/point (a). In (b) is a 1 Å/point scan of the 100 Å square region in the front corner of (a).

Fig. 12 Shaded view and cross section of a surface region of a 4000 Å thick film, showing a steep, narrow canyon.

contradictions is by postulating many small voids in the material, with H atoms bonded to the Si at these void surfaces. NMR and SAXS studies cited in the Introduction suggest that we actually are dealing with such an inhomogeneous material. The character of these voids may be crucial to the electronic properties and photovoltaic stability of these films, and finding the causes of void formation during film growth is a major concern. Although our data show incipient voids on the surface of this material, we have not attempted to measure a void density from these data. The nature of our data does not allow for estimates of the volume of our incipient voids, nor whether they might be filled by further film growth. Finally, it should be noted that the recorded data are biased by interest in certain features and are therefore not valid for a statistical sampling. Here we report the first observations of the atomic-scale topography over large areas of this growing surface of a device-quality film. (Prior STM studies concentrated on H-atom bonding at the surface, based on tunneling barrier height, and in both cases heavily p-doped films were studied. In Ref. 13 the surface was also Ar^+ bombarded before tunneling.)

It is well established that a-Si:H film growth from silane glow discharge results predominantly from SiH_3 radical reactions with the film surface.²¹⁻²³ These radicals diffuse through SiH_4 gas to arrive at the surface in a cosine distribution, so they strike protruding regions of the surface more frequently than low regions. If they reacted and remained at the point of arrival, this microscopic shadowing would inevitably lead to a highly porous, filamentary and useless film.²⁴ Since this is not observed, then either radical surface diffusion before incorporation occurs or energetic surface ion bombardment compacts the top layers of the growing film. Although such bombardment occurs for some deposition conditions, the highest (electronic) quality films are often grown under low-power glow-discharge conditions that yield minimal energetic bombardment. Thus, it is clear that considerable SiH_3 surface diffusion must occur, and moreover that this diffusion must be accompanied by some degree of preferential incorporation in valleys as opposed to hilltops. On the other hand there appear to be many small voids in the final film, so this diffusion and preferential incorporation apparently fails to fill in many low regions before they are covered over. Understanding and ultimately controlling this void growth is a primary concern.

All models of the film growth have so far been homogeneous reaction-chemistry models, yet film inhomogeneities appear to be common and crucial. Other important, unsuspected factors must cause this inhomogeneous growth. To search for clues, the present study has surveyed many areas of a number of films and film thicknesses. We have looked for differences as well as patterns, and found both. The most common surface shape found on fully-developed films ($\geq 1000 \text{ \AA}$ thickness) was continuous rounded hills with height/width < 0.2 , gradually sloping sides and relatively flat connecting valleys. The surfaces of the larger hills ($\sim 100 \text{ \AA}$ height, $\sim 1000 \text{ \AA}$ width) were often covered with finer hills, but again with low height/width and slopes. No incipient voids are indicated in such regions, although those of $< 20 \text{ \AA}$ size would probably have been missed due to our probe resolution.

Several major variations on the above "gentle rolling hill" regions were found. In some regions steep sided, small ($\sim 50 \text{ \AA}$ wide) hills were observed, with narrow, steep pits

suggesting incipient voids at their intersections (Fig. 9). Steep-sided canyons through other regions clearly indicate long, connected incipient voids (Fig. 12). These might even have been the edge of an internal void surface. One unusually large hill (~ 300 Å high, ~ 2000 Å wide, not shown here) was observed on an otherwise relatively flat area, suggesting a 300 Å tall microparticulate transformed with the probe tip. This and many smaller but relatively steep-sided hills (e.g. Fig. 9) might be attributed to silicon microparticulates deposited from the discharge, if we assume that these can conduct the STM current or be covered by a conducting film. On the other hand, any region that can sustain more rapid than average growth through a number of layers will produce a similar isolated-hill, particularly as seen with our present STM resolution.

The most surprising deviations from the overall hilly character of the fully-developed (≥ 1000 Å) surface were the very smooth regions. These areas were observed to have at most a few atomic layers of height variation across hundreds of Å in lateral dimensions (e.g. Fig. 10 and 11). Generally, this was a smooth surface on a large, gently sloping hill (e.g. Fig. 10(a)), rather than a nearly constant film thickness. These areas appear extremely homogeneous and free of voids (of ≥ 10 Å size), and if the entire film had this character it might have superior properties. These areas are not crystalline, as a-Si:H does not grow microcrystals under our deposition conditions.²⁵ Very effective SiH_3 diffusion and valley-filling is demanded to explain the existence of such regions. But if this is true, then other factors are required to explain the failure to smooth out other areas. This dichotomy of smooth versus steep, hilly areas on the same surface is uniquely demonstrated by Fig. 11, where the border between such a smooth and a hilly region was captured.

We have so far observed with moderate probe resolution relatively few a-Si:H films, all deposited under a single set of discharge conditions. Although limited, these data nonetheless support the model of SiH_3 diffusion and preferred valley incorporation, at least in many areas of the surface. However, these observations also show that the film surface is highly inhomogeneous, suggesting that other crucial factors are playing a role in the growth of film-voids and inhomogeneities. It is tempting to conjecture on possible causes, to see if these might suggest ways to improve the photovoltaic quality and stability of intrinsic a-Si:H. We offer a few ideas here.

(1) In order to produce the (> 20 Å wide) structural inhomogeneities observed here, an irregularity at one surface atomic site or in one surface region must influence the growth of many overlying atomic layers; it cannot be buried and restored to normal by the next Si-layer. This might be achieved by a surface impurity that has enhanced reactivity for SiH_3 , but only if the incorporation reaction frequently transfers the impurity up to the new surface. This might be possible for surface-bonded OH or NH_2 radicals, for example. The average impurity concentration in intrinsic a-Si:H films is $\sim 10^{18}/\text{cm}^3$, far more than needed to induce reported void densities, but most studies of intrinsic a-Si:H electronic properties suggest minimal correlation with impurity concentrations (for reasonably low values).

(2) Crystal growth rates often vary considerably in different directions and at step edges, and such orientation effects might also occur for SiH_3 reactions with H covered film. The short-range order in a-Si:H may be sufficient to maintain effective orientations across nm scale distances, and this could lead to unequal growth rates over a similar thicknesses range. This could combine with incomplete diffusional compensation of shadowing effects to yield many small voids.

(3) One of the most obvious potential causes of small voids is a nonreactive surface site. (A CH_3 attached to a Si surface atom is a well-known example in a-Si:C:H alloy films; the CH_3 is usually buried intact.²⁶) Shadowing will tend to expand and propagate this void upward through successive Si layers, while SiH_3 diffusion counters this. Only in the unlikely event that reactivity at adjacent sites is also lowered should this lead to more than a very small void, essentially enclosing the nonreactive site.

(4) Microparticulates, which are presumed chemically similar but electronically different than the film, can form in the discharge and bond to the surface.^{27,28} It is unlikely that SiH_3 diffusion is sufficient to fill in the gaps below and adjacent to such particulates, so voids of comparable size would probably result. However, these particulates become negatively charged once they reach perhaps 10 Å size, and their charge combined with the plasma potential then tends to keep them away from the substrate. Also, particulates have not been detected in low power, high flow discharges such as used here.

None of the above conjectures offers feasible explanations of the canyon-like incipient voids we detected (Fig. 12). These suggest an entire void surface reaching down into the film, or at least a cord-like void. This appears to require the coalescence of many void activators (impurities?), or a non-reactive boundary between growing regions. Although this looks somewhat like a finer-scale form of "columnar" films,^{29,30} we do not think these are directly related. Those columnar films were grown in very different discharges under "physical deposition" conditions, where shadowing effects dominate and minimal SiH_3 deposition occurred. Perhaps, in the present case, impurities tend to coalesce into such regions, preserving diminished growth rates. SiH_3 incorporation on surfaces facing the plasma might be enhanced relative to inside deep canyons, causing small voids to grow laterally as well as upward with additional layers.

Conclusions

This STM-based investigation of a-Si:H surface topographies has discerned a variety of film characteristics that appear significant to its electronic properties and stability. Perhaps the most surprising and important observation is significant film inhomogeneity found by comparing different surface regions; the films appeared to be a multi-phase material. Void regions appeared to be clustered, with some appearing at the surface as a line, as might be expected for a grain boundary. Other surface areas were very flat, and the lateral size of surface hills varied between regions. We could only conjecture, from this initial study using one set of deposition conditions, what might be responsible for these film variations.

However, the mere existence of extremely smooth and almost atomically flat surface regions supports the SiH_3 diffusion and valley-filling model, and also offers a tantalizing hope that it might be possible to produce more homogeneous and perhaps better photovoltaic material.

A significant difference was observed between 100 Å thick films and the thicker films. The thin films show no sign of islanding, particulates, or void structures, and appeared much like the smoothest regions of the thicker films. This suggests that some changes in the character of the discharge may occur after the first few minutes of operation, perhaps due to the film resistivity or even particulate growth. Another useful result of this study is a demonstration of the ability to vacuum tunnel into intrinsic a-Si:H without damaging the material. Occasional atomic transfers between sample and probe and tunneling gap fluctuations clearly occurred, but reproducible topographies were generally obtained.

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