Bond Selectivity in Silicon Film Growth

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Hydrogen atoms can selectively eliminate strained bonds that form during the growth of amorphous silicon films. By periodically interrupting the growth and exposing the grown material to hydrogen, the film composition can be varied continuously from a non-equilibrium amorphous structure to that of a crystalline solid. Furthermore, by tuning the hydrogen exposure it is possible to discriminate between Si–Si bonds formed on different substrates, thereby allowing substrate-selective growth. The evolution of the film structure during hydrogen exposure is directly observed by scanning tunneling microscopy, and a model describing the role of hydrogen is presented.

The ability to tailor structural and electronic properties is a fundamental goal of materials science. This necessitates the development of techniques that allow direct control of the chemical bonding in materials. Such capabilities are particularly important in non-equilibrium systems where, in addition to the preferred equilibrium geometry, there exist other accessible bonding configurations. Despite the fact that their structure is often poorly controlled, non-equilibrium materials are of great technological importance. For example, plasma-assisted low-temperature growth of silicon (Si) from silane yields hydrogenated amorphous silicon (a-Si:H), which is used extensively in solar-cell and flat-panel display applications (*1*). Since non-equilibrium properties are introduced during growth, control of the growth kinetics is a prerequisite for material design. We introduce a scheme that allows us to directly manipulate the growth chemistry on a bond-by-bond basis. By exploiting the ability of hydrogen atoms to selectively eliminate strained bonds, we can control the non-equilibrium character of materials. In the case of low-temperature Si, exposure of the growth surface to hydrogen atoms allows continuous control of the structure from that of an amorphous material to one that is crystalline. Furthermore, by tuning the hydrogen exposure we can selectively grow Si on some substrates while eliminating it from other substrates exposed to the same growth conditions (*2*).

The Si films were grown in a radio-frequency (rf) plasma-deposition system (13.56 MHz) in which separate hydrogen and silane (doped with 1% phosphine) inlet gases were used. The silane gas inlet was electronically controlled to allow time modulation of the silane flow, whereas hydrogen flowed continuously into the plasma and decomposed into atoms. The use of this pulsed scheme allowed the repeated growth of a film of predetermined thickness followed by a controlled exposure to hydrogen atoms. Typical growth conditions were: H_2 flow, 100 sccm (standard cubic centimeters per minute); SiH_4 flow, 20 sccm; rf power, 100 W (160 mW/cm^2); and pressure, 300 mtorr. The substrate deposition temperature was 275°C throughout. Scanning tunneling microscopy (STM) analysis was performed in vacuum on freshly prepared films following a 1% HF etch of the surface. Other HF concentration were used with similar results. This HF treatment removes any trace oxidation that occurs prior to insertion into the vacuum system and leaves the surface in a passivated state (*3*, *4*).

An STM image of a 700 Å thick Si film that was deposited on a metallized (500 Å Mo) Si(111) substrate is shown in Fig. 1A. The metal layer was used to eliminate any possible influence on the growth chemistry by the Si substrate. The film was grown under continuous silane-flow deposition conditions. The surface is seen to be homogenous and smooth; the root-mean-square (rms) roughness is 5.1 Å. The Raman spectrum obtained from this film (Fig. 2A) consists of a broad feature centered at ~480 cm^{-1}. This spectrum is characteristic of a-Si:H (*5*); the energy and width of the peak reflect a distribution of Si bonding environments in the film. Since the sp^3 bonding configuration in crystalline Si is thermodynamically preferred, the distribution observed in spectrum A indicates the presence of strained bonds within the film.

The results shown in Figs. 1A and 2A are not dependent on the type of substrate used. This is consistent with the fact that low-temperature Si growth produces uniform nucleation and ultimately the formation of a randomly bonded Si network, independent of the substrate (*6*). The technological importance of this material is derived from the former property, which allows large-area deposition, whereas the latter determines the electronic properties of devices fabricated from this material.

An STM image of a 700 Å thick Si film grown with the pulsed deposition technique is shown in Fig. 1B. The substrate used was identical to that in film A. By gating the silane flow, a thin layer of conventional material was deposited over a period of 5 s followed by a 50-s exposure to hydrogen atoms. Note that the conditions during the deposition cycle are identical to those used in the growth of film A. However, in contrast to the homogenous appearance of A, film B is very textured; the rms surface roughness is 18.5 Å. In the Raman spec-

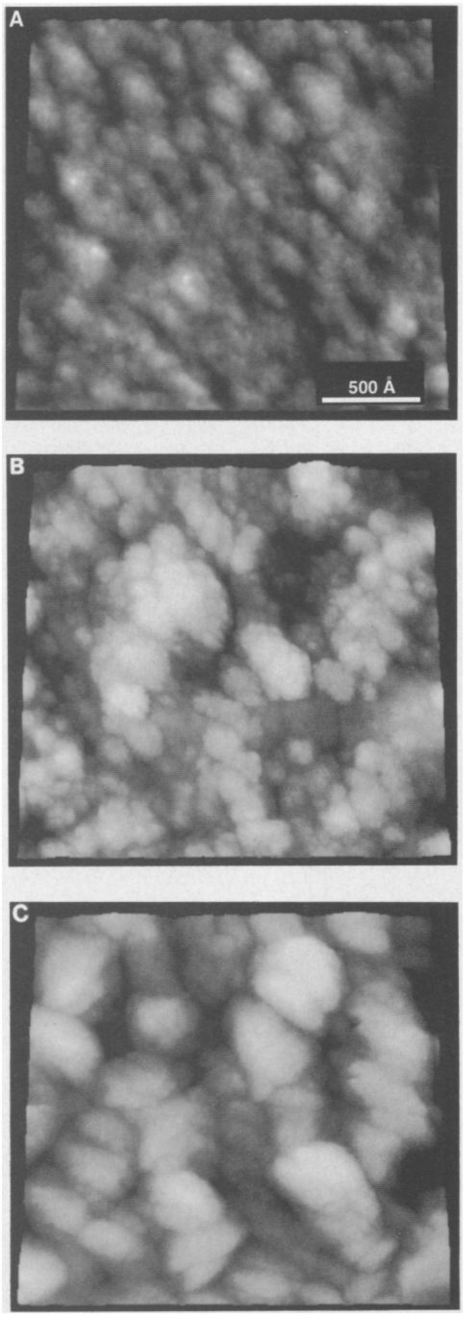

Fig. 1. Scanning tunneling microscope images of 700 Å–thick Si films grown during a hydrogen exposure cycle of (**A**) 0, (**B**) 50, and (**C**) 200 s. The duration of the growth cycle was 5 s in (B) and (C) while the actual growth conditions were the same throughout. Each image is 2400 Å by 2400 Å and was recorded with a sample bias of +3 V. The rms surface roughness is (A) 5.1, (B) 18.5, and (C) 28.3 Å.

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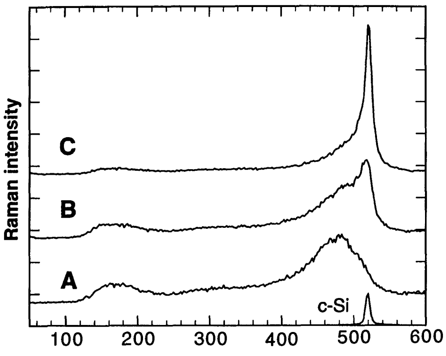

Fig. 2. Raman spectra recorded from the 700 Å thick Si films grown with the use of a hydrogen exposure cycle of: (A) 0, (B) 50, and (C) 200 s. The excitation wavelength was 4765 Å, and a crystalline Si reference spectrum recorded under the same condition is also shown.

trum obtained from this film (Fig. 2B) the broad amorphous feature has been dramatically reduced and the spectrum now contains a narrow, higher frequency peak centered at ~520 cm^{-1}. This peak is characteristic of bulk Si (5), and the frequency shift is consistent with the greater strength of Si–Si bonds in the bulk environment. Evidently, without changing the growth conditions it is possible to enhance the film crystallinity by a controlled exposure to hydrogen atoms during growth. Note that this behavior is independent of the actual growth conditions; the crystallinity of any non-equilibrium Si film can be improved with this modulation technique (7).

In order to demonstrate our ability to control the film crystallinity, Fig. 1C shows an STM image of a 700 Å Si film grown with an extended hydrogen exposure cycle. The conditions during the deposition cycle are identical to those in films A and B. The rms surface roughness is now 28.3 Å, and the average feature size has increased and exhibits what appears to be a well-defined grain structure. The Raman spectrum obtained from this film is dominated by the narrow crystalline peak (Fig. 2C); the amorphous shoulder is now almost entirely eliminated. By tuning the hydrogen exposure we can control the composition of the film in a continuous fashion, ranging from a non-equilibrium amorphous structure to that of a crystalline solid.

The ability of hydrogen atoms to control the chemical bonding within the film can be readily understood in terms of the growth kinetics. Under normal growth conditions, adsorbed silane species have limited surface mobility and nucleation occurs more or less uniformly over the entire surface, which is consistent with the growth morphology seen in Fig. 1A. Therefore, silane species reacting with the growth surface do not necessarily bond in an optimal fashion and yield a variety of Si–Si bonding configurations. Some of these bonds are bulklike, whereas others are highly strained. Under continuous growth conditions, this bond distribution persists and is incorporated into the film, as evidenced by Raman spectrum A. However, repeated interruption of the deposition after the growth of a thin layer of material allows hydrogen to manipulate the growth chemistry. Earlier, we showed that hydrogen is capable of discriminating between bonds on the basis of strain (8). Strained bonds are weaker and more susceptible to reaction and elimination by hydrogen. Atom-resolved STM studies of crystalline Si (9) and Ge surfaces (8) have shown that this elimination process occurs in three steps. First, hydrogen is inserted into strained Si–Si bonds, which results in the formation of relaxed film precursors (8, 9). Second, the precursors diffuse over the surface facilitated by the flux of hydrogen atoms (10). Finally, when a precursor encounters a favorable binding site, H_2 is eliminated and an unstrained Si–Si bond is formed (11). Hydrogen catalyzes the transformation of strained Si–Si bonds into bulklike bonds. The extent of this transformation is controlled by the duration of the hydrogen exposure. The presence of distinct nucleation sites is responsible for the clustered-growth morphology observed in Fig. 1B. In the absence of favorable binding sites the precursors are eventually removed from the surface, particularly during long hydrogen exposures.

The results described above are applicable to any substrate. Silicon deposited at low temperature has a distribution of bonding geometries and it should always be possible to find conditions that selectively eliminate the more highly strained bonds. However, there are differences between the Si nuclei formed on different substrates. Each substrate has it own particular arrangement of surface atoms that determine its ability to nucleate Si film growth. It is possible to use this modulated growth technique to tune the hydrogen exposure to discriminate between Si–Si bonds formed on different substrates. This is evident from Fig. 3, which shows the growth rate as a function of hydrogen exposure for a series of different substrates. Uniform growth is initially observed on all substrates, which is consistent with the nonselective nature of low-temperature Si growth. However, by increasing the hydrogen exposure time the growth rate on the Al substrate drops off precipitously. A similar behavior is observed on the SiO_2 and sapphire substrates at longer exposures. The ability of hydrogen to selectively eliminate growth is due to differences in the strengths of the Si–Si bonds which make up the nuclei on different substrates. In general, more strongly bound nuclei are formed on crystalline substrates (sapphire versus SiO_2) or those that readily form silicides (Mo versus Al) (2, 12). Crystalline Si, as expected, is an ideal substrate, and growth is still observed following extended hydrogen exposures. However, the growth rate slowly decays with increasing exposure, reflecting the ability of hydrogen to eliminate even bulklike Si–Si bonds (2, 9).

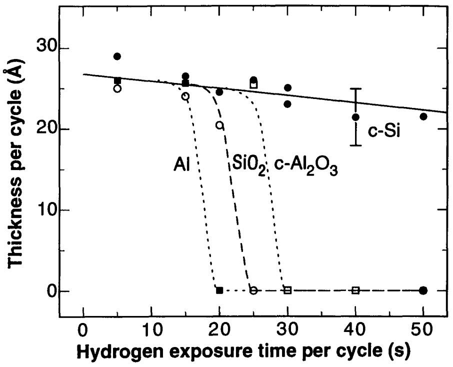

Fig. 3. Average thickness of material deposited per growth cycle as a function of the duration of the hydrogen exposure cycle for a series of different substrates: Al (■), c-Si (●), SiO_2 (○), and c-Al_2O_3 (□). The duration of the growth cycle was 10 s. throughout, and growth was accumulated for 40 deposition-exposure cycles. The error bars are associated with the nonzero thickness values and represent the typical distribution of measured film thicknesses. Data points at zero thickness indicate no observable film growth. The solid line is a linear fit to the data including points not shown at 200-s exposure time.

Based on the data in Fig. 3, it is possible to tune the hydrogen exposure to allow selective growth on one or more substrates. This ability has particular significance for device fabrication, which typically involves a series of photomask and vacuum-deposition steps. However, the substrate-selective growth chemistry allows some of the device patterning to be done in situ, thereby reducing the number of photomask steps and minimizing interface exposure and contamination. We have used this selective process to fabricate high-performance thin-film transistors, demonstrating its feasibility for device applications (12).

This modulation technique manipulates the growth kinetics by exploiting the ability of hydrogen to preferentially react with weak bonds and to enhance the mobility of film precursors on the surface. Note that this method promotes the growth of kinetically resilient materials and not necessarily the thermodynamically favored material. In the case of Si these are one and the same. However, hydrogen plays an important role in many growth environments. For instance, hydrogen atoms promote diamond-film growth by eliminating the more readily etched graphitic nuclei (13). Here kinetically resilient diamond is preferentially formed over the thermodynamically favored graphite structure. As in the case of Si, it is likely that a more controlled exposure to hydrogen atoms will allow additional flexibility in the growth of these and other non-equilibrium materials.

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Isotope Effect in Superconducting Fullerenes

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The effect of isotopic substitution on the superconducting transition temperature, T_c, in alkali-doped C_{60} has been examined. Paradoxically, it is found that a substantial decrease in T_c with the increasing isotopic mass is possible even when the attractive interaction is not mediated by phonons but is instead of purely electronic origin. In particular, it is shown that the experimentally measured isotopic shifts are consistent with a recently proposed electronic mechanism. Further predictions are presented that can be tested by experiment.

Measurement of the isotope shift of the superconducting transition temperature, T_c, was one of the classic experiments (*1*) that established the essential role of the electron-phonon interaction in those simple metallic superconductors that are well described by the theory of Bardeen, Cooper, and Schrieffer (BCS). In this report, we wish to examine this effect in a new light—that is, in the context of a recently proposed electronic mechanism of the superconductivity of doped fullerenes (*2, 3*). We demonstrate that such a mechanism can lead to an isotope effect, and the observed magnitudes of δT_c are consistent with microscopic estimates we make in the context of the electronic mechanism (*4*). Moreover, we make further predictions of the pressure and the dopant species dependence of the isotope shift that are susceptible to experimental test.

The isotope effect is conventionally characterized by an exponent x, where $T_c \propto M^{-x}$, where M is the mass of the isotope. Recent experiments have led to widely differing values of x, ranging from 0.3 to 1.8 in Rb-doped C_{60} (*5, 6*). (It is important to note that such a power law dependence, while natural in the context of the conventional BCS theory, is not self-evident. A better characterization is the ratio $\delta T_c/T_c$, where δT_c is the shift of the transition temperature upon isotopic substitution. For Rb_3C_{60} with $T_c \approx 30$ K, values of δT_c have been reported by different groups ranging from -0.5 to -1.5 K.) As has been already noted (*5*), it is difficult to obtain an $x > 0.5$ in the context of a conventional electron-phonon mechanism. From the discussions given in this report, it follows that no such natural upper bounds exist for the proposed electronic mechanism for the superconductivity of fullerenes.

In the proposed electronic mechanism for superconductivity in doped C_{60}, we have computed the effective attraction, E_p, between electrons at an average electron density of three extra (conduction) electrons per molecule. Once the strength of the attraction is determined, T_c can be estimated in accordance with mean-field theory,

$$T_c \propto W \exp\{-W/E_p\} \qquad (1)$$

Here W is the inverse of the density of states at the Fermi energy (which is proportional to the intermolecular bandwidth) and hence characterizes the hopping rate of the electrons between molecules. Undoubtedly, the prefactor in this equation will be modified by fluctuation effects, but we expect the exponent to be correct as long as the BCS mean-field theory of superconductivity is approximately valid. Because the isotope effect that we shall derive depends predominantly on the exponent, we can use this simple equation with impunity. Note, of course, this expression is valid only as long as E_p is positive. The important question is how does the pair-binding energy E_p depend on isotopic substitution?

For M_3C_{60}, where M is the alkali dopant, E_p is given by (*3*)

$$E_p \approx -0.05U + 0.015\frac{U^2}{t} + \ldots$$

$$= AU\left(\frac{U}{t} - x_c\right) + \ldots, \qquad (2)$$

where $A = 0.015$ and $x_c = 3.4$ and U is the effective Coulomb repulsion on a carbon atom in the C_{60} molecule. The hopping matrix element t characterizes the delocalization of a π-electron on the molecule. Actually, there are two such matrix elements—one for the bonds on the pentagons t, and one for the bonds connecting the pentagons t'. It is believed (*7*) that $1.0 < t'/t < 1.3$. In the above expression we have set $t'/t = 1.2$, although similar expressions are known over the whole range of t'/t (*2, 3*). The above approximate expression is the result of second-order perturbation theory in U/t. However, if there exists a critical value of U/t denoted by x_c at which E_p becomes positive, then in the neighborhood of x_c, the dependence of E_p on U/t is linear. That an attractive effective interaction is not an artifact of second-order perturbation theory has been amply demonstrated by exact numerical calculations on smaller clusters (*8*) and, indeed, the shifts in x_c due to higher order terms are generally found to be small. The precise value of the pair-binding energy depends on the precise values of U and t, which are only known approximately. [As discussed earlier (*2, 3*), we expect U to be of order 5 to 10 eV and t to be between 2 to 3 eV.]

Clearly, for there to be an isotope dependence of T_c, E_p (equivalently t) or W must depend on the isotopic mass. In general, we expect that there will be a mass dependence of t: as a function of increasing M the zero-point fluctuations of the carbon atoms decrease; hence the mean separation between the atoms decreases, in much the same way that the lattice constant of a solid decreases with decreasing temperature. As the separation l between the carbon atoms decreases, t increases, so we expect t to be an increasing function of M. Thus, it is easy to see from Eqs. 1 and 2 that T_c decreases as M increases, provided W remains constant.

It could also be argued that the reduction of the carbon-carbon bond length on a given molecule could give rise to a decrease of the lattice constant of the solid, which,

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