PHYSICAL REVIEW B VOLUME 56, NUMBER 15 15 OCTOBER 1997-I

Film growth and surface reactions of C_{60} on Si(100)H(2×1)

J. Schmidt, M. R. C. Hunt, P. Miao, and R. E. Palmer
Nanoscale Physics Research Laboratory, School of Physics and Space Research, The University of Birmingham,
Birmingham B15 2TT, United Kingdom

(Received 16 April 1997)

High-resolution electron-energy-loss spectroscopy (HREELS) has been used to characterize C_{60} films up to 4 monolayers thick grown at room temperature on hydrogen-terminated Si(100). Our results show that compared with C_{60} films on clean Si(100) surfaces a considerably higher degree of order in the as-deposited films is achieved. At low coverages the observed C_{60} vibrational modes and the Si-H vibrations of the substrate are essentially unshifted, indicating a van der Waals–type interaction between C_{60} and Si(100)H(2×1). After annealing at 450 K the film order is substantially increased. Annealing at 600 K results in desorption of the C_{60} multilayers and a hydrogen-transfer reaction from the surface to the adsorbed monolayer molecules. When annealing the sample at 800 K, the remaining surface terminating hydrogen desorbs and evidence for a change in the C_{60} bonding configuration is found. Finally, flashing the sample at 1300 K leads to the formation of silicon carbide. [S0163-1829(97)09039-5]

I. INTRODUCTION

C_{60} and its relatives, the so-called fullerenes, have attracted wide interest since their discovery in 1985 and have been studied extensively because of their unique physical and chemical properties (for a recent review see Ref. 1). Currently, studies of the nature of fullerene film growth are of particular interest. The bonding of fullerenes to solid surfaces is often complicated, so phenomena such as charge transfer between substrate and adsorbate, chemical reactions, orientational ordering and reconstruction of adsorbate and/or substrate may be expected.

Recent scanning tunneling microscopy (STM) and combined high-resolution electron-energy-loss spectroscopy–low-energy electron diffraction (HREELS-LEED) investigations of C_{60} films grown on semiconducting substrates show that well-ordered films can be achieved. Deposition of C_{60} on GaAs(110) at room temperature leads at low coverages to ordered monolayer islands, which exhibit a linear molecular arrangement commensurate with the GaAs substrate with a compressed next-neighbor distance of 9.8 Å compared to 10.04 Å for closed packed C_{60}.[2] The existence of these islands as observed in STM demonstrates that C_{60} possesses a high surface mobility on GaAs, attributed to a weak van der Waals interaction with the substrate. C_{60} multilayer structures grown on GaAs(110) at room temperature consist of highly corrugated three-dimensional islands commensurate with the substrate, whereas film growth at 450 K yields almost perfectly ordered C_{60} layers with (111) orientation.[3] Gensterblum *et al.*[4–6] observed epitaxial growth of fcc C_{60} films on layered semiconductor substrates such as GaSe and GeS, to which C_{60} is also bound by the weak van der Waals interaction. On GaSe(0001) at low coverages (up to 3 ML) and substrate temperatures of about 150 °C ordered C_{60}(111) films were found; thicker films grow in polycrystalline form as indicated by the disappearance of the LEED diffraction pattern at higher coverages.[4,5] Films grown on GeS(001) at a substrate temperature of ≈200 °C are almost perfectly crystalline for thicknesses up to 1000 Å (Refs. 4–6) due to the almost perfect lattice match between GeS(001) and C_{60}(111) (lattice mismatch only ≈0.75%). After room temperature deposition on GeS no LEED pattern was observable, postgrowth annealing at 200 °C resulted in ordered films of similar quality to those observed after high-temperature growth.

Growth of epitaxial C_{60} films on silicon surfaces is of particular interest for technological reasons. At room temperature on clean Si(100)(2×1) surfaces the strong interaction between the C_{60} molecules and the substrate induces film growth in the Stranski-Krastanov mode; the first monolayer only shows local order.[7–11] A C_{60} (4×3) quasihexagonal structure, with a lattice mismatch of 4% compared with the bulk C_{60} fcc (111) surface, coexisting with a $c(4\times4)$ arrangement, has been observed in STM studies by Hashizume *et al.*[12] and Wang and co-workers.[13] Thicker films on Si(100)(2×1) are composed of orientationally disordered three-dimensional islands. Hebard *et al.*[14] have grown C_{60} films up to 1000 Å in thickness by room-temperature sublimation onto Si(100) and Si(111) substrates that have been passivated by dipping in hydrofluoric acid, resulting in a saturation of the surface dangling bonds with hydrogen. The saturation of the Si dangling bonds with H leads to van der Waals bonding of adsorbates. X-ray diffraction measurements reveal that films deposited on such substrates have a high degree of crystallinity. Recently Dumas *et al.*[15] carried out HREELS and multiple infrared reflection spectroscopy investigations of C_{60} deposition on wet-chemically prepared Si(111)H(1×1) surfaces. HREELS measurements showed that good quality films were obtained despite the comparatively large lattice mismatch of 11.5%. However, details of the bonding properties of C_{60} on hydrogen-terminated silicon surfaces, in particular questions concerning the interaction strength and possible surface reactions, are left unresolved. Si is one of the most important materials in electronic device fabrication and semiconductor physics, so that an understanding of the interaction of C_{60} with different Si surfaces is especially important.

In this paper, we report on HREELS investigations of the growth of C_{60} films with coverages between 0.5 and 4 ML on hydrogen terminated Si(100) surfaces at room temperature and subsequent annealing to various elevated temperatures. The results show that for room temperature adsorption highly ordered C_{60} films can be grown and the substrate-adsorbate interaction is of van der Waals character. After annealing at 450 K an increased order in the deposited films was found. At 600 K a part of the surface terminating hydrogen bonds to the C_{60} molecules. Further annealing leads to a simultaneous breaking of the C-H and remaining Si-H bonds. The substrate-adsorbate interaction before and after annealing is different: a change in the bonding configuration after annealing at 800 K is found; at this point all surface terminating H has desorbed. After flashing the sample to ≈ 1300 K the molecules decomposed and reacted with the Si atoms to form silicon carbide.

II. EXPERIMENT

The experiments were carried out in a multichamber UHV system consisting of a load-lock chamber, a preparation chamber, and an analysis chamber equipped with a high-resolution electron energy-loss spectrometer, an Auger electron spectrometer, a three-grid LEED optics, a quadrupole mass spectrometer for residual gas analysis, and a gas inlet system. The analysis chamber was pumped by a turbomolecular pump, an ion getter pump, and a liquid-nitrogen–cooled titanium sublimation pump. After baking out a base pressure of about 1×10^{-10} mbar was achieved, the residual gas being mostly hydrogen. Sample heating was performed by electron bombardment from the back of the crystal. Temperature was measured with a NiCr-Ni thermocouple attached to the sample holder, which in a separate experiment was calibrated against a thermocouple directly clamped onto a Si sample. The Si(100) substrates were n-type ($\rho > 15\ \Omega$ cm), samples were approximately $12\times10\times0.5$ mm in size. Clean Si(100)(2×1) surfaces were prepared by first outgassing the samples for several hours at about 900 K in the preparation chamber. After transfer into the analysis chamber the samples were flashed to around 1400 K for 30 s at a pressure around 5×10^{-9} mbar. Surface cleanliness was monitored with Auger electron spectroscopy. The as-prepared samples showed a clear (2×1) LEED pattern. Atomic hydrogen was produced by cracking H_2 ($p\approx 2\times10^{-6}$ Torr) on a hot Ta strip mounted in front of the gas line outlet approximately 10 cm away from the sample. During exposure the sample was held at about 600 K in order to avoid the formation of dihydride or trihydride phases.[16] A dose of 1200 L ($1\ \mathrm{L}=10^{-6}$ Torr s) H_2 was found to be sufficient to produce a saturation coverage of H on the surface. A (2×1) LEED pattern was found after H dosing, indicative of a Si-H monohydride phase on the surface as confirmed by subsequent EELS measurements. C_{60} was deposited from a Knudsen cell held at 425 °C with the substrate at room temperature. The thickness of the deposited films was determined from the ratio of the Si 92 eV to the C 272 eV Auger peaks calibrated for a monolayer coverage of C_{60} after annealing a multilayer at temperatures above 700 K. A thickness of 7 Å is estimated as 1 ML of the C_{60} film. All EELS measurements were made at 300 K sample temperature. Vibrational spectra were obtained with a primary beam energy of $E_0=4.5$ eV and with a resolution (full width at half maximum of the elastic peak) between 2.5 and 4 meV. Spectra of electronic excitations were recorded with degraded resolution (approximately 20 meV) at 20 eV primary energy.

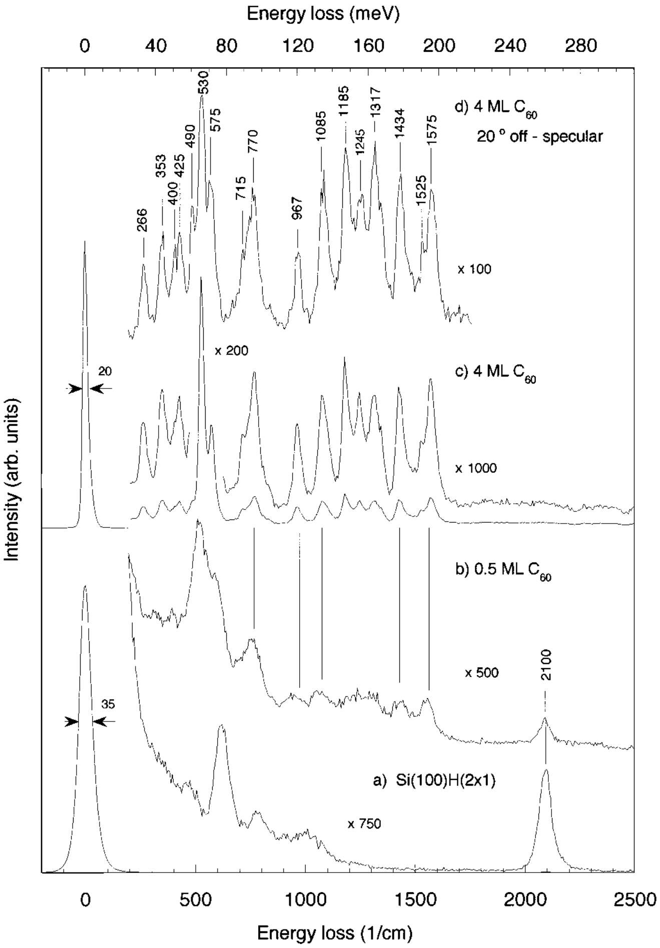

FIG. 1. HREELS spectra showing vibrational excitations of (a) clean Si(100)H(2×1) and deposited C_{60} layers; (b) 0.5 ML, and (c) 4 ML C_{60}. Primary energy $E_0=4.5$ eV, FWHM of the elastic peak 35 cm^{-1} in spectra (a) and (b), 20 cm^{-1} in spectrum (c). Spectra (a)–(c) were taken in specular scattering geometry with $\theta_i=\theta_f=55°$. Spectrum (d) shows a spectrum of a 4 ML film taken in off-specular geometry ($\theta_i=35°$, $\theta_f=55°$) with $E_0=5$ eV, FWHM of the elastic peak 20 cm^{-1}. All spectra are normalized to the elastic peak.

III. RESULTS AND DISCUSSION

A. C_{60} film growth

Figure 1(a) shows an electron energy-loss spectrum of the vibrational excitations of the Si(100)H(2×1) substrate surface. The two dominant losses at 620 and 2100 cm^{-1} are due to the bending and stretching vibration of Si-H monohydride species, respectively.[17] The three weak peaks found at about 450, 750 and 1000 cm^{-1} can be assigned in order of increasing energy to the rocking mode, the symmetric stretching mode and the asymmetric stretching mode of a Si-O-Si species,[18] which probably stems from incomplete desorption of the native surface oxide during preparation of the Si(100)(2×1) surface prior to the hydrogen termination.

After deposition of 0.5 ML C_{60} in Fig. 1(b) several C_{60} related losses appear in the energy range from about 400 to 1600 cm^{-1}, well-defined peaks are found at 530, 770, 970, 1085, 1435, and 1575 cm^{-1}. On the high-energy side of the intense 530 cm^{-1} loss a shoulder at 575 cm^{-1} is observed and a broad loss structure in the range from $\approx$ 1200 to 1300 cm^{-1} is found.

The high symmetry of C_{60} leads to a strong degeneracy of its vibrational modes: C_{60} possesses 14 optical active modes (4 threefold degenerate dipole-active modes of T_{1u} symmetry and 10 Raman-active modes of H_g and A_g symmetry) and 32 optically inactive modes.[19] The peaks observed at 530, 575, and 1435 cm^{-1} correspond well with dipole-active modes found at 530, 580, and 1440–1450 cm^{-1} in previous HREELS investigations on thick C_{60} films, the latter with a possible contribution from a Raman active H_g mode found at the same frequency.[5,7,8] The losses at 1085 and 1575 cm^{-1} are Raman-active modes (H_g), the 770 cm^{-1} loss has possibly contributions from a H_g and G_u mode found at 775 and 760 cm^{-1}, respectively. In IARS and Raman spectroscopy and the 970 cm^{-1} loss is ascribed to a G_u mode (see Table I). In contrast with HREELS results for a C_{60} monolayer deposited on clean Si(100)(2×1),[20] where no distinct dipole losses could be observed and the Raman-active peaks were dominant in the spectra, the 530 cm^{-1} dipole-active mode generates by far the most prominent loss in Fig. 1(b).

The intensity of the Si-H stretching vibration in Fig. 1(b) is substantially smaller than the corresponding peak in Fig. 1(a), whereas its frequency is essentially unchanged.

With increasing C_{60} coverage (the corresponding spectra are not shown in the figure) the C_{60} related losses become more pronounced and the intensity of the Si-H stretching vibration is further diminished. At a coverage of about 1 ML, the loss structure at around 1100 cm^{-1} is resolved into three different peaks at 1185, 1245, and 1317 cm^{-1}. The 1185-cm^{-1} mode was also previously observed with HREELS on thick films[5,7,8] and ascribed to a dipole-active vibration of the C_{60} molecule.

Figure 1(c) shows the HREELS spectrum of a 4-ML-thick film; additional peaks at 266, 353, and 425 cm^{-1} are found. Several new losses appear as shoulders on more intense peaks: loss features are found on the low-energy sides of the 1575 cm^{-1} mode and the 770 cm^{-1} mode at about 1525 and 715 cm^{-1}, respectively. In previous HREELS investigations[5,7,8] of C_{60} films the 575 cm^{-1} dipole-active mode was only observed as a weak shoulder on the 530 cm^{-1} loss; in the spectra of Fig. 1(c) this loss is clearly resolved. Off-specular measurements prove both peaks are dipole active as their intensities follow closely the intensity of the elastic peak as the off-specular angle is increased. The results of off-specular measurements for the 1185 and 1434 cm^{-1} losses are inconclusive due to their comparatively small intensities. A spectrum measured 20° off-specular is displayed in Fig. 1(d). The 530 and 575 cm^{-1} peaks are roughly an order of magnitude smaller than in Fig. 1(c), whereas the 1185 and 1434 cm^{-1} losses show only little change. Due to the strong decrease in intensity of the T_{1u} mode at 530 cm^{-1}, a new peak at 490 cm^{-1} can be resolved, additionally a loss at 400 cm^{-1} is found on the low-

TABLE I. Comparison between observed vibrational frequencies of C_{60} on Si(100)H(2×1) with literature values for thick C_{60} films.

	This investigation	IRAS, Raman	HREELS
	Frequency $\omega_i(cm^{-1})$		
		Even parity	
$\omega_1(A_g)$		498[a,b]	
$\omega_2(A_g)$		1470[a,b]	
$\omega_1(T_{1g})$		502[a,b]	
$\omega_2(T_{1g})$		976[a,b]	960[d]
$\omega_3(T_{1g})$		1358[a,b]	
$\omega_1(T_{2g})$		567[a,b]	581[d]
$\omega_2(T_{2g})$		865[a,b]	
$\omega_3(T_{2g})$		914[a,b]	
$\omega_4(T_{2g})$		1360[a,b]	
$\omega_1(G_g)$	490	486[a,b]	
$\omega_2(G_g)$		621[a,b]	
$\omega_3(G_g)$		806[a,b]	
$\omega_4(G_g)$	1085	1076[a,b]	1073[d]
$\omega_5(G_g)$		1356[a,b]	
$\omega_6(G_g)$	1525	1525[a,b]	
$\omega_1(H_g)$	266	273[a,b]	274[c,d]
$\omega_2(H_g)$	425	433[a,b]	436,[d]444[c]
$\omega_3(H_g)$	715	711[a,b]	758[c,d]
$\omega_4(H_g)$	770	775[a,b]	758[c,d]
$\omega_5(H_g)$	1085	1101[a,b]	1097[c,d]
$\omega_6(H_g)$	1245	1251[a,b]	1258,[c]1274[d]
$\omega_7(H_g)$	1434	1427[a,b]	1436,[d] 1452[c]
$\omega_8(H_g)$	1575	1578[a,b]	1557,[d] 1565[c]
		Odd parity	
$\omega_1(A_u)$		1143[a,b]	
$\omega_1(T_{1u})$	530	527[a,b]	532[c,d]
$\omega_2(T_{1u})$	575	576[a,b]	581[d]
$\omega_3(T_{1u})$	1185	1183[a,b]	1186[d]
$\omega_4(T_{1u})$	1434	1429[a,b]	1436,[d] 1452[c]
$\omega_1(T_{2u})$	353	356[a,b]	347,[d] 355[c]
$\omega_2(T_{2u})$		680[a,b]	686[c]
$\omega_3(T_{2u})$		1026[a,b]	
$\omega_4(T_{2u})$		1201[a,b]	
$\omega_5(T_{2u})$	1575	1576[a,b]	
$\omega_1(G_u)$	400	400[a,b]	347,[d] 355[c]
$\omega_2(G_u)$		760[a,b]	
$\omega_3(G_u)$		924[a,b]	
$\omega_4(G_u)$	967	970[a,b]	960,[d] 968[c]
$\omega_5(G_u)$	1317	1310[a,b]	
$\omega_6(G_u)$		1446[a,b]	1436,[d]1452[c]
$\omega_1(H_u)$		343[a,b]	
$\omega_2(H_u)$		563[a,b]	
$\omega_3(H_u)$		696[a,b]	686[c]
$\omega_4(H_u)$		801[a,b]	
$\omega_5(H_u)$		1117[a,b]	
$\omega_6(H_u)$		1385[a,b]	
$\omega_7(H_u)$		1559[a,b]	

[a] Reference 21.
[b] Reference 22.
[c] Reference 8.
[d] Reference 5.

energy side of the 425 cm^{-1} loss. The energies of the peaks observed in Fig. 1(d) together with their assignment to the different C_{60} vibrational modes are summarized in Table I.

Comparison between the spectra in Fig. 1 shows that at submonolayer C_{60} coverages neither the Si-H stretching vibration nor the C_{60} related losses are significantly shifted compared to the clean Si(100)H(2×1) surface and the thick C_{60} film, respectively. This strongly points to a van der Waals–type interaction between the C_{60} molecule and the hydrogen-terminated Si(100) surface. Using infrared spectroscopy Dumas *et al.*[15] observed a downward shift of the Si-H stretching frequency on Si(111)H(1×1) of about 20 cm^{-1} with increasing C_{60} coverages, and a concomitant increase of the linewidth from 0.8 to 10 cm^{-1} while the total integrated intensity of the line remained constant. On Si(100)H(2×1) a frequency shift and broadening of the peak similar to those observed on Si(111)H(1×1) can be anticipated, but with a resolution of 35 cm^{-1} in Fig. 1(b) cannot be resolved in our experiments.

Lucas[23] has shown that due to the broadening in angle of the so-called dipole lobe with increasing film disorder the intensity of the dipole-active vibrational modes decreases relative to the intensity of the Raman-active modes. Thus the ratio of the intensities of the dipole- and Raman-active modes can be used as a measure of the long-range order in the film. For the highest-quality films obtained until now [grown on GeS(001) at elevated substrate temperatures] an intensity ratio of 23 between the 530 and 760 cm^{-1} losses was found.[4,5] On Si(111)H(1×1) ratios of 15 and 12 were found for deposition at $T \geqslant 150\,°C$ and room temperature, respectively.[15] From Fig. 1(d) an intensity ratio of 11 can be extracted, very much in accordance with the results on H-terminated Si(111) for deposition at room temperature. With LEED only a diffuse uniform background could be detected in our experiments.

The minimal change in the film quality despite the much smaller lattice mismatch of Si(100)H(2×1) compared with Si(111)H(1×1) might reflect the fact that the wet-chemical preparation method produces a nearly perfect, unreconstructed H-terminated Si(111) surface,[24,25] whereas it is known that even on well-prepared Si(100)(2×1) surfaces a substantial number of missing dimer defects (5%) exist, which might act as additional nucleation sites in the growth of C_{60} films on the hydrogen-terminated (100) surface. Furthermore, in contrast to the atomically flat Si(111)H(1×1) surface the dimerized Si(100)(2×1) surface is strongly corrugated. In order to form an ordered monolayer the C_{60} molecules have to overcome the corrugation potential due to the Si dimer rows; this process might be kinetically hindered at room temperature.

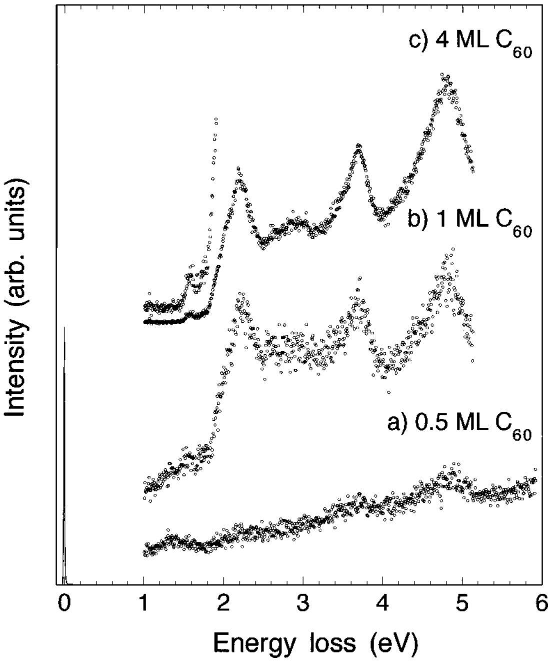

FIG. 2. HREELS spectra of the low-energy electronic excitations of C_{60} films grown on Si(100)H(2×1) at room temperature; (a) 0.5 ML, (b) 1 ML, and (c) 4 ML of C_{60}. Primary energy $E_0=20$ eV, $\theta_i=\theta_f=55°$. The spectra are normalized to the elastic peak.

Figure 2 shows spectra of the low energy electronic excitations of C_{60} films of 0.5, 1, and 4 ML thickness. The multilayer film spectrum Fig. 2(c) shows features at 1.55, 2.2, 3, 3.7, and 4.8 eV previously observed on thick C_{60} films on Si(100)(2×1).[7,8,23] The 1.55 eV loss is attributed to the triplet exciton (the lowest-lying exciton level in C_{60}) and the loss band from 1.8 to 2.2 eV is due to adsorption in the singlet exciton manifold. The rather undefined weak structure around 3 eV and the peaks 3.6 and 4.7 eV are due to one-electron π-$\pi^\star$ transitions in the C_{60} molecule. Comparison of spectra (a) and (b) for films in the submonolayer regime with the spectrum (c) shows that all features observed for the thick film are essentially unchanged (taking the different signal-to-noise ratios into consideration). This is further proof of a van der Waals–type interaction between C_{60} and the Si(100)H(2×1) surface.

B. Annealing of C_{60} films

Room-temperature adsorption of C_{60} on Si(100)H(2×1) can be explained in terms of a van der Waals–type interaction, as discussed in the previous section. It was expected, therefore, that annealing our sample to higher temperatures would result in desorption of the adsorbates, in contrast to the results on clean Si(100), where the adsorbate-substrate interaction is so strong that the molecules decompose before desorption. EELS spectra obtained as a function of sample temperature following the growth of a about 1.5 ML thick C_{60} film at room temperature are displayed in Figs. 3(a)–3(e).

After annealing the room-temperature deposited film for 5 min at 450 K [Fig. 3(a)] the intensiy ratio between the 530 and 760 cm^{-1} losses increased from 9 for the as-deposited film to 13 after annealing, indicating an increased film order. Furthermore, the intensities of the dipole-active modes at 1185 and 1434 cm^{-1} exhibit a pronounced increase compared with the Raman-active modes in the same frequency range. Post-deposition annealing of a room-temperature deposited film on GeS at 500 K showed similar effects: after annealing, the film quality was identical to the case of high-temperature deposition.[5] The relative increase in the intensity ratio with annealing found for C_{60} on Si(100)H(2×1) in this study is much larger than the difference between room-temperature deposition and deposition at a substrate tempera-

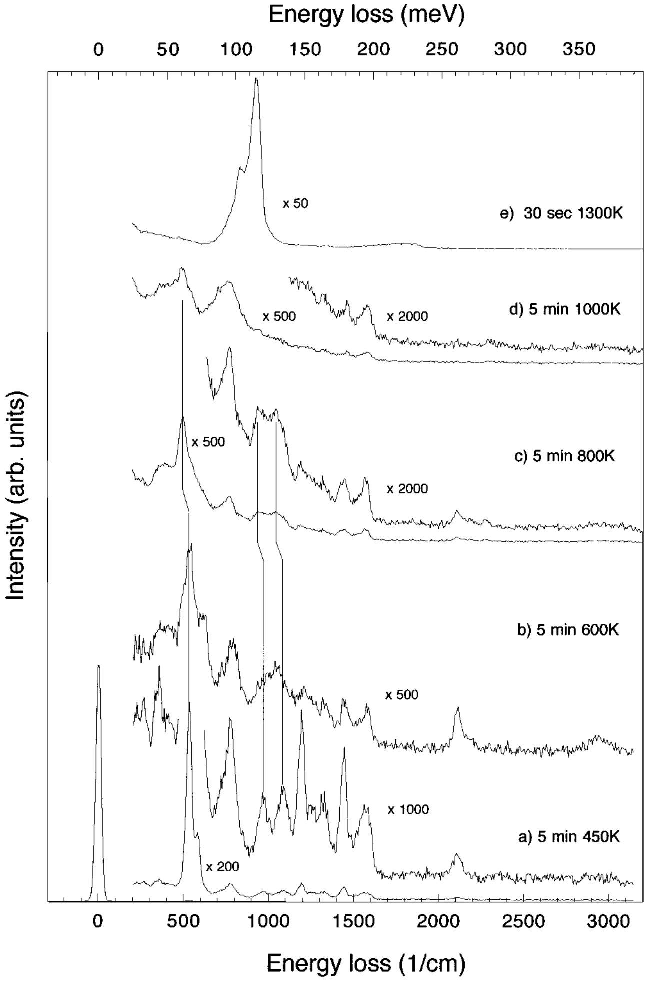

FIG. 3. HREELS spectra recorded after annealing a 1.5 ML-thick C_{60} film at (a) 450 K, (b) 600 K, (c) 800 K, (d) 1000 K, and (e) 1300 K for the times indicated. Primary energy $E_0 = 4.5$ eV, $\theta_i = \theta_f = 55°$. The spectra are normalized to the elastic peak.

ture of 150 °C on Si(111)H(1×1) observed by Dumas *et al.*[15] This observation strongly supports the argument brought forward in Sec. III A, that the essentially identical film quality after room-temperature growth on Si(100)H(2×1) and Si(111)H(1×1), despite the smaller lattice mismatch on Si(100), is primarily due to the corrugation of the Si(100)H(2×1) surface.

After annealing the film at 600 K the C_{60} related part of the spectrum is very similar to that observed after deposition of 1 ML C_{60} at room temperature, in particular, the Si-H related loss at 2100 cm^{-1} is present in both spectra. Auger spectroscopy on the annealed sample confirms that after heating to 600 K around 1 ML of C_{60} is left on the surface; the C_{60} multilayers desorb. Multilayer desorption at 600 K was also observed by Hamza and Balooch[26] for C_{60} films on clean Si(100)(2×1) substrates. The detection of a C_{60} monolayer after annealing a thick film is clear evidence that the adsorbate-substrate interaction for C_{60} on Si(100)H(2×1) is stronger than the adsorbate-adsorbate interaction, despite the van der Waals character of the former. In contrast to the results on silicon surfaces, annealing C_{60} films grown on GeS(001) at temperatures above ≈ 550 K leads to sublimation of all the C_{60} molecules.[5] The interaction of C_{60} with clean Si(100)(2×1) was discussed by Sarid and Chen,[10] who postulated a dipole–induced dipole interaction between the Si(100)(2×1) surface and C_{60} molecules at temperatures below 870 K due to the electric dipole moment associated with the charge transfer from the up to the down atom in the buckled dimers of the (2×1) reconstruction. On hydrogen-terminated Si(100) the dimers are no longer tilted but become symmetric, so that the dimer-related surface dipoles are removed. However, H termination leads to the formation of Si-H dipoles since hydrogen is more electronegative than silicon, so the picture of the interaction of surface dipoles with induced dipoles in the adsorbed C_{60} molecules may still apply.

In contrast to the results obtained after deposition of a monolayer of C_{60} at room temperature, in Fig. 3(b) a small but clearly visible loss due to C-H stretching vibrations is observed at about 2930 cm^{-1}. This peak is certainly not due to hydrocarbon contamination on the surface: in previous investigations it has been found that CH contaminants desorb at about 450 K from C_{60} films.[5] The appearance of CH species indicates that a thermally activated hydrogen transfer reaction takes place; some of the surface-terminating hydrogen atoms bond to C_{60} molecules at elevated temperatures. It is known that individual C_{60} molecules are highly reactive towards free-radical addition and readily form covalent bonds with atomic hydrogen. Mass spectrometric studies of the hydrogenation of C_{60} performed by the exposure of C_{60} films to atomic hydrogen[27] prove the formation of C_{60} H_n species with $n = 2$ to > 24. In accordance with our results, investigations of the reaction of atomic H with C_{60} in a cyclohexane matrix using Fourier transform infrared spectroscopy (Ref. 28) show bands at 2855 and 2825 cm^{-1} with the infrared active C_{60} modes at 530, 575, 1185, and 1434 cm^{-1} essentially unchanged. First-principles density-functional calculations of C_{60} H indicate that the stable state has H attached to one C atom outside the C_{60} molecule. The bonding of a H atom replaces a double C=C bond with a C–H bond.[29] The calculations also give a lower limit for the C_{60}-H binding energy of 0.3 eV. Using empirical hydrocarbon potentials[30,31] binding energies of ≈ 2 eV per H atom were obtained. An intuitive value for the binding energy would be between 0.3 eV and 4–5 eV, a typical figure for alkanes.

With increasing temperature the Si-H and C-H stretch related peaks become smaller at about the same rate. The C_{60}-H bonding energy is therefore probably comparable to the Si-H bonding energy of 3.9 eV, in line with the discussion above, which might explain why only partial hydrogen transfer occurs from the substrate to the adsorbed C_{60} molecules. Simultaneously with the decrease of the SiH and CH losses a broadening of the T_{1u} mode at 530 cm^{-1} takes place together with a shift of its center towards lower frequencies. Additionally, frequency shifts and a change in the relative intensities of the modes at 967 and 1087 cm^{-1} are observed.

In Fig. 3(c) after annealing at 800 K, the peaks related to the Si-H and C-H stretching vibration have essentially disappeared and a significant shift of the frequency of the dipole active T_{1u} mode from 530 cm^{-1} in Fig. 3(b) to 500 cm^{-1} and of the 967 and 1087 cm^{-1} modes by around 40

cm^{-1} towards lower frequencies is found. The remaining C_{60} losses are unchanged and AES spectra show an unchanged amount of C on the surface.

Thermal desorption of the surface terminating hydrogen with simultaneous dehydrogenation of the C_{60} molecules and bonding of the C_{60} to the bare silicon surface could explain these results. In thermal-desorption spectroscopy hydrogen desorption from silicon surfaces is observed at about 850 K close to the annealing temperature used in Fig. 3(c). The observed frequency shifts and intensity changes in the HREELS spectra are probably indicative of a change in the C_{60} bonding configuration: STM investigations of Chen and Sarid[10] have shown that after annealing at 870 K a transition in the bonding state of adsorbed C_{60} molecules from weak physisorption at bonding sites between the silicon dimer rows to strong chemisorption on top of the dimer rows takes place. In the STM experiments of Chen and Sarid the sample was annealed for only 10 s at 870 K. Taking the much longer annealing times (300 s) used in our experiments into consideration a change of the bonding configuration for the adsorbed C_{60} molecules even at 800 K seems plausible. Significant changes in the vibrational spectra have been observed previously for C_{60} monolayers chemisorbed on metal surfaces.[32,33] The frequency shifts and accompanying intensity variations are related on the one hand to a charge transfer between the substrate and the C_{60} adsorbate, while on the other hand the distortion of the C_{60} molecules due to the hybridization between the C_{60} molecular orbitals and the metal substrate states has to be taken into account.

We tentatively ascribe the observed frequency shifts of the 530 cm^{-1} $T_{1u}(1)$ mode and of the losses at 970 $[T_{1g}(2)]$ and 1085 cm^{-1} $[H_g(5)/G_g(4)]$ to the combined effect of charge transfer from the Si substrate to the C_{60} and a distortion of the adsorbed C_{60} molecules due to the formation of a strong bond with the substrate.

In the HREELS experiments of Hunt[20] an increase of the intensity of the 760 cm^{-1} mode relative to a loss structure centered around 900 cm^{-1} was found after annealing a monolayer of C_{60} on Si(100)(2×1) at 870 K. The latter peak was ascribed to a C_{60} mode enhanced by the interaction with the clean silicon substrate and is absent in the spectra taken on hydrogen-terminated surfaces, most likely due to the strongly reduced adsorbate-substrate interaction. Unfortunately, in the experiments of Ref. 20, because of the comparatively poor resolution and intense background present in the spectra (both primarily a result of the high doping level in the Si substrate), the 530 cm^{-1} dipole loss could not be resolved at monolayer coverages and appeared only as a weak shoulder on the high-energy side of the elastic peak; thus information about peak shifts cannot be reliably extracted from the data. An increase in the relative intensity of the 760 cm^{-1} mode as observed by Hunt after annealing at about 900 K is observed in our experiments after annealing at 1000 K in Fig. 3(d). We ascribe this effect to an increased roughness in the monolayer film and the onset of fragmentation of C_{60} molecules.

After flashing the sample to 1300 K the spectrum again changes significantly and two new very intense peaks appear at 830 and 930 cm^{-1} in Fig. 3(e). The dominant 930 cm^{-1} loss was also observed in HREELS investigations of β-SiC(100) by Dayan[34] and attributed to the excitation of Fuchs-Kliewer surface phonons. The weaker loss at 830 cm^{-1} is close to the frequency of the Si-C stretching vibration in surface silicon carbide formed at the surface by pyrolysis of CH groups. These results demonstrate that at high temperatures the C_{60} cages break up and silicon carbide is formed, as previously observed by Hamza and Balooch[35] and Sarid and Chen.[36]

IV. SUMMARY

We have used high-resolution electron-energy-loss spectroscopy to investigate C_{60} film growth on hydrogen-terminated Si(100) surfaces.

For thin films of up to 1 ML C_{60} coverage the Si-H stretching vibration and the C_{60} related losses are observed at essentially the same frequencies as for the clean Si(100)H(2×1) surface and for thick C_{60} films, respectively, indicating a van der Waals–type interaction between C_{60} and Si(100)H(2×1). The dominance of the dipole-active losses at 530 and 575 cm^{-1} over the Raman-active mode at 760 cm^{-1}, which is prominent in spectra of C_{60} on clean Si(100)(2×1), proves that the film is well ordered. Annealing of the as-deposited films at temperatures below 450 K leads to an increase in film order, indicative of a kinetic hindrance of the film growth at room temperature due to the corrugation of the Si(100)H(2×1) substrate surface potential. After annealing at 600 K a monolayer of C_{60} is left on the surface; the adsorbate-substrate interaction for C_{60} on Si(100)H(2×1) is obviously stronger than the intermolecular interaction. Evidence for hydrogenation of the adsorbed C_{60} is found; hydrogen atoms are liberated form the surface and bond to the C_{60} molecules. Further annealing leads to a simultaneous breaking up of the C-H bonds in the hydrogenated C_{60} molecules and the remaining Si-H bonds with the surface and desorption of the hydrogen atoms. Frequency shifts and changes in the relative intensities of a number of C_{60} related losses in the HREELS spectra are found after annealing at 800 K, when all the surface-terminating hydrogen has desorbed, and are interpreted as a signature of a change in the C_{60} bonding configuration from comparatively weak bonding at low temperatures to strong chemisorption at higher temperatures. At about 1000 K decomposition of the adsorbed molecules sets in. Flashing the sample at 1300 K leads to the formation of silicon carbide.

ACKNOWLEDGMENTS

We are grateful to Dr. A. W. Robinson for his help in setting up the experimental system. J.S. would like to thank the Lloyds of London Tercentenary Foundation for financial support. M.R.C.H. is grateful to the Leverhulme Trust and The University of Birmingham for support. P.M. would like to thank The University of Birmingham for financial support. This work was supported by the EU via an HCM network (Contract No CHRX-CT94-0580) and by the EPSRC, Grant No GR/K71431.

---

[1] See, for example, *Solid State Physics*, edited by H. Ehrenreich and F. Saepen (Academic Press, New York, 1994), Vol. 48.

[2] Y. Z. Li, J. C. Patrin, M. Chandler, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Science **252**, 547 (1991).

[3] Y. Z. Li J. C. Patrin, M. Chandler, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Science **253**, 429 (1991).

[4] G. Gensterblum, J. J. Pireaux, P. A. Thery, R. Caudano, Ph. Lambin, and A. A. Lucas, J. Electron Spectrosc. Relat. Phenom. **64/65**, 835 (1993).

[5] G. Gensterbulm, L.-M. Yu, J. J. Pireaux, P. A. Thiry, R. Caudano, J.-M. Themlin, S. Boudizi, F. Coletti, and J.-M. Debever, Appl. Phys. A **56**, 175 (1993).

[6] J.-M. Themlin, S. Boudizi, F. Coletti, J.-M. Debever, G. Gensterblum, L.-M. Yu, J. J. Pireaux, P. A. Thiry, and R. Caudano, Phys. Rev. B **46**, 15 602 (1992).

[7] G. Gensterblum, J. J. Pireaux, P. A. Thery, R. Caudano, J. P. Vigneron, Ph. Lambin, and A. A. Lucas, Phys. Rev. Lett. **67**, 2171 (1991).

[8] A. Lucas, G. Gensterblum, J. J. Pireaux, P. A. Thiry, R. Caudano, J. P. Vigneron, Ph. Lambin, and W. Krästschmer, Phys. Rev. B **45**, 13 694 (1992).

[9] S. Suto, O. Ikeno, N. Horiguchi, Y. Achiba, T. Goto, and Y. Nishina, J. Electron Spectrosc. Relat. Phenom. **64/65**, 877 (1993).

[10] D. Sarid and D. Chen, Surf. Sci. **329**, 206 (1995).

[11] T. Sakurai, Prog. Surf. Sci. **51**, 263 (1996).

[12] T. Hashizume, X.-D. Wang, Y. Nishina, H. Shinohara, Y. Saito, Y. Kuk, and T. Sakurai, Jpn. J. Appl. Phys., Part 1 **31**, L880 (1992).

[13] X.-D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, and T. Sakurai, Phys. Rev. B **47**, 15 923 (1993).

[14] A. F. Hebard, O. Zhou, Q. Zhong, R. M. Fleming, and R. C. Haddon, Thin Solid Films **257**, 147 (1995).

[15] P. Dumas, M. Gruyters, P. Rudolf, Y. He, L.-M. Yu, G. Gensterblum, R. Caudano, and Y. J. Chabal, Surf. Sci. **368**, 330 (1996).

[16] J. J. Boland, Surf. Sci. **261**, 17 (1992).

[17] R. Butz, E. M. Oellig, H. Ibach, and H. Wagner, Surf. Sci. **147**, 345 (1984).

[18] H. Ibach, H. D. Bruchmann, and H. Wagner, Appl. Phys. A **29**, 113 (1982).

[19] D. E. Weeks and W. G. Harter, Chem. Phys. Lett. **144**, 366 (1987).

[20] M. R. C. Hunt, J. Phys. Condens. Matter **8**, L229 (1996).

[21] Z. H. Dong, P. Zhou, J. M. Holden, P. C. Eklund, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **48**, 2862 (1993).

[22] K. A. Wang, A. M. Rao, P. C. Eklund, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **48**, 11 375 (1993).

[23] A. A. Lucas, J. Phys. Chem. Solids **53**, 1415 (1992).

[24] Y. J. Chabal, P. Dumas, P. Guyot-Sionnest, and G. S. Higashi, Surf. Sci. **242**, 524 (1991).

[25] G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, Appl. Phys. Lett. **56**, 656 (1990).

[26] A. V. Hamza and M. Balooch, Chem. Phys. Lett. **201**, 404 (1993).

[27] P. A. Brühweiler, S. Anderson, M. Dippel, N. Mårtensson, P. A. Demirev, and B. U. R. Sundqvist, Chem. Phys. Lett. **214**, 45 (1993).

[28] J. A. Howard, Chem. Phys. Lett. **203**, 540 (1993).

[29] S. K. Estreicher, C. D. Latham, M. I. Heggie, R. Jones, and S. Öberg, Chem. Phys. Lett. **196**, 311 (1992).

[30] B. I. Dunlap, D. W. Brenner, J. W. Mintmire, R. C. Mowrey, and T. C. White, J. Phys. Chem. **95**, 5763 (1991).

[31] K. Breadmore, R. Smith, A. Richter, and B. Mertesacker, J. Phys. Condens. Matter **6**, 7351 (1994).

[32] M. R. C. Hunt, S. Modesti, P. Rudolf, and R. E. Palmer, Phys. Rev. B **51**, 10 039 (1995).

[33] S. Modesti, S. Cerasari, and P. Rudolf, Phys. Rev. Lett. **71**, 2469 (1993).

[34] M. Dayan, Surf. Sci. **149**, L33 (1985).

[35] A. V. Hamza and M. Balooch, Surf. Sci. **317**, L1129 (1994).

[36] D. Sarid and D. Chen, Nanotechnology **7**, 153 (1996).