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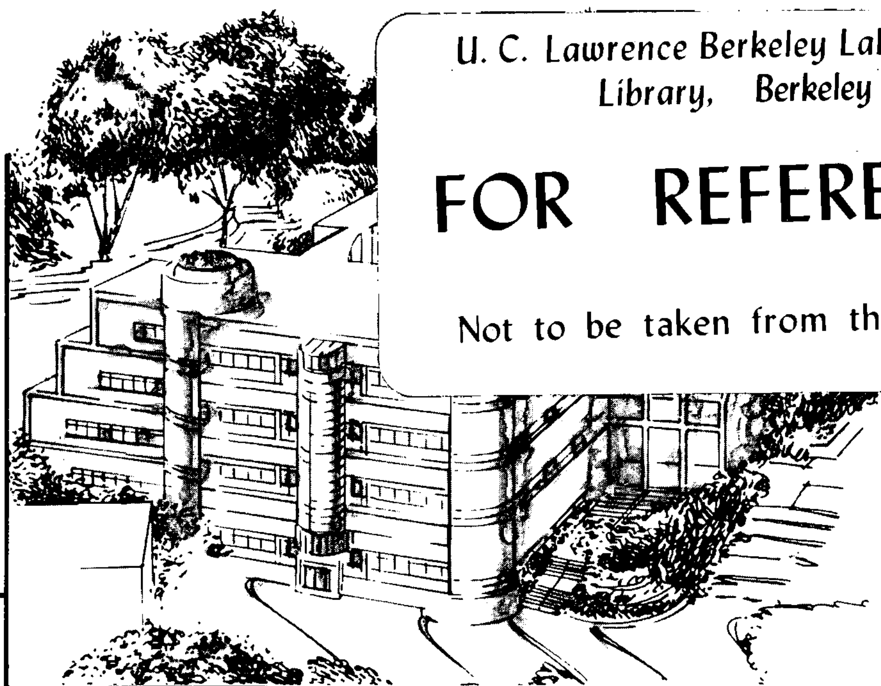

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X-ray Reflectivity Measurements of the Expansion of Carbon Films upon Annealing.

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Abstract.

Measurements have been made of the x-ray reflectivity from ultra thin, amorphous carbon films both before and after annealing. Analysis of the x-ray results indicates that annealing causes an increase in film thickness with a corresponding decrease in density. Such behaviour is uncharacteristic of amorphous thin films and is interpreted as being due to changes in the interatomic bonding associated with transition to a more graphitic microstructure.

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In recent years there has been considerable interest in the properties of amorphous carbon thin films due to a number of unique and useful properties that they possess. In particular, their high hardness, chemical inertness, optical transparency and lack of magnetic response makes them ideal as protective coatings for magnetic and optical disks.[1] Carbon films can be prepared and treated in a variety of ways, resulting in different physical and chemical properties and these have been the source of extensive theoretical and experimental study.[2-5] Ultra-thin carbon films have also become important as integral components of nanometer period multilayer structures, used to provide significantly enhanced x-ray reflectance in many x-ray optical applications. The thermal stability of such structures critically affects their performance, particularly for use in synchrotron x-ray beams where considerable heating can occur.[6] Specifically, measurements of metal/carbon multilayers show an increase in the multilayer period after annealing[7] and this has been attributed to compound formation at the interfaces, crystallisation of the metal and possible expansion of the carbon layer.[8-11] In this paper we report on x-ray reflectivity measurements of thin carbon films, both prior to and after annealing. The specularly reflected x-ray intensity is dependent on the refractive index, and hence electron density changes at and near the sample surface.This has been illustrated by several studies of thin-film materials, both in the solid and liquid phase.[12,13] Analysis of the measurements enables accurate determination of film thickness, density and interface roughness.

Carbon thin film samples were prepared by dc magnetron sputtering of a graphite target onto polished silicon substrates (40x10x6mm thick), which were carefully cleaned by standard methods prior to deposition. Different thicknesses of carbon were deposited by controlling the speed and number of revolutions of the substrates, which were rotating approximately 100mm above the target. During deposition the argon sputter gas pressure was 2.5×10^{-3} torr and the power was 1000W. The substrates were at room temperature before deposition although the temperature was not controlled during the sputtering process. Three different thicknesses of carbon film were prepared, nominally 400Å, 200Å and 50Å, the thickness being estimated from the sputtering time.

The x-ray reflectivity experiments were performed using a four-circle Huber goniometer based on a Rigaku 12kW rotating anode x-ray generator with a copper target. $CuK\alpha_1$ x-rays (λ= 1.54051Å) were selected and collimated by reflection from the (111) planes of a germanium monochromator crystal followed by a slit to eliminate the $CuK\alpha_2$ component. The monochromatic beam was then incident on the sample and the scattered intensity was measured by a scintillation counter after passing through a slit. For high count-rates callibrated Al filters were used to attenuate the scattered beam. With the diffractometer in this configuration the resolution function in the x-ray scattering plane is determined by the finite divergence of the incident beam and the width of the detector slit. The width of the slit was fixed at 0.5mm. Measurements were performed on the as-deposited samples in the form of θ-2θ scans, i.e. scans along the specular reflectivity rod in reciprocal space. Similar scans, at a constant angular offset in θ, 0.3°, from the specular peak were used to obtain a background count-rate which was subtracted from the data. The experimental technique has been described in detail elsewhere.[13,14]

After measurement the samples were annealed in a vacuum of 10^{-6} torr at 600°C for 4 hours and then the reflectivity measurements were repeated. No attempt was made to control surface contamination either before or after annealing and the reflectivity experiments were performed in air. Figures 1-3 show the x-ray reflectivity data for the nominally 400Å, 200Å and 50Å thick films respectively, (a)before and (b)after annealing. The reflectivity is normalised such that the incident beam intensity is 1 and the data from the annealed samples are displaced by two orders of magnitude. Measurement of the reflected intensity below 0.3° was unreliable due to the footprint of the incident beam being larger than the sample surface. The modulation in the reflectivity arises from interference between x-rays scattered from the carbon/air and carbon/silicon interfaces and hence the period of this oscillation is directly related to the thickness of the carbon film.[14] The most obvious effect of annealing is to cause an increase in the oscillation frequency corresponding to an increase in film thickness.

The reflection of x-rays from a layered, dielectric medium was discussed by Parratt in 1954 who derived a recursion formula to calculate the reflected intensity from successive interfaces.[15]

The theory was modified to include the effects of surface roughness[16] and has been used successfully in a number of studies.[17,18] Obtaining quantitative information from the reflectivity data proceeds by supposition of an electron density profile with N discreet dielectric layers, each layer being described by four parameters:electron density, thickness, roughness and linear absorption coefficient. These parameters can then be adjusted in calculations of the reflectivity which are compared with the measured data. For the carbon/silicon system the effects of absorption are negligible and the absorption coefficients were fixed at the theoretical value for carbon.

Although the period of the oscillations in each curve in figures 1-3 could be matched using a model with only a single carbon film on silicon, the observed intensity could not be reproduced. In fact, good fits to the data could only be obtained by the addition of two other layers to the model, one at the sample surface and one at the C/Si interface. The fits to the data with this 3 layer model are shown by the solid lines in figures 1-3 according to the parameters in Table I (Figs.1-3(a) the as-deposited samples) and Table II (Figs.1-3(b) the annealed samples). The refractive index has been converted to mass density using the approximation $\rho=7.35\times10^{8}\ \delta/\lambda^{2}$, where δ is the real part of the complex refractive index and λ is the x-ray wavelength in Ångstroms.[13] In addition to the parameters shown, the calculated reflectivity was convoluted with a Gaussian function representing the instrumental resolution[19] and multiplied by an overall scale factor which was found to be slightly less than 1. The unannealed carbon film density we obtain is slightly higher than that obtained in other measurements of sputtered carbon films.[3] For comparison,the density of diamond is 3.52 gcm^{-3} and that of graphite is 2.27 gcm^{-3}.

The presence of an additional layer at the sample surface is not surprising and was observed in previous x-ray reflectivity measurements of carbon films.[13] No attempt was made during the experiment to control surface contamination and it is likely that this layer is due to absorbates such as water and other organic material. It is also well known that silicon forms a native oxide SiO_x and it is possible that this could be represented by the layer at the C/Si interface. However, the density of the interfacial layer, layer 1 in Tables I and II, is low compared to that

obtained in previous measurements of silicon wafers, which indicated that the oxide was within 5% of the silicon substrate density.[20,21] The origin of this layer is, therefore, not fully understood, although it is possible that it may represent a low density region in the carbon film as it bonds to the silicon substrate. It should be noted that without either of the additional layers in the model it was not possible to obtain good fits to the data. This is due to the sensitivity of x-ray reflectivity to the microscopic details of the sample structure, especially when the measurements occur over such a large angular and dynamic range.

The primary differences in the data prior to and after annealing result from changes in the carbon film. This can be seen by comparing the parameters in Tables I and II. For each thickness of carbon film annealing causes an expansion, with a corresponding decrease in film density. The product $\rho_C d_C$, also shown in the tables, is constant, indicating that mass is conserved in the expansion process. Little change in the properties of the other layers is observed. Reflectivity measurements sample the in-plane electron density averaged over the coherence length of the x-ray beam. Conservation of mass therefore means that the expansion, which is of the order 6-8%,is directed along the surface normal. The magnitude of this effect is consistent with the results of experiments on mutilayer systems[7-11] but it is the first time that such detailed measurements of thickness and density changes have been obtained from a single carbon film.The conservation of mass implies that these annealing-induced changes represent actual changes in the average interatomic structure of the films, and are not simply the result of the evolution of gaseous species.

It is generally expected that annealing amorphous, thin films would cause an increase in density associated with interatomic rearrangements towards an equilibrium bonding arrangement characterized by a more closely packed, possibly crystalline structure. Measurements of a-C:H films similarly showed annealing to cause a reduction in volume due to the loss of hydrogen and the disappearance of an as-deposited void structure.[22] However, the carbon films studied here exhibit a significant decrease in density on annealing, contrary to these expectations. The effect of annealing on carbon films has been studied by Raman spectroscopy[23,24] and is characterised by changes in the intensity ratio and positions of the D and G lines. These Raman results were

interpreted as being due to a change in the film from an amorphous to a more graphitic structure, consistent with the removal of bond angle disorder and possibly driven by the formation of graphite microcrystals. This interpretation is in good agreement with our x-ray results and indeed, Raman spectra of our samples taken before and after annealing showed identical behaviour to the published data.[25] As-deposited carbon films are characterized by an amorphous network having a relatively large fraction of bonding defects compared to pure sp^2 (graphitic) bonding. Some of these bonding defects may be of sp^3 (diamond -like) character, yielding locally dense regions. Annealing causes a shift to a larger fraction of sp^2 bonds, perhaps nucleated by the formation of graphite microcrystals. These bonding rearrangements cause an average density decrease and an expansion of the film perpendicular to the substrate, both of which are directly observed in our x-ray reflectivity measurements. Presumably, with this expansion in the film, and assuming good adhesion at the substrate, compressive stresses in the plane of the film may develop.

In summary, x-ray reflectivity is an accurate method for determining the thickness, density and roughness of thin carbon films. The changes in the thickness and density of these films upon annealing at 600°C are of the order 6-8% and are easily detectable.The observed thickness increase and density decrease conserve mass within the films studied, and can be understood as resulting from changes in interatomic bonding from a defective as-deposited amorphous network towards a more graphitic structure. Further studies to correlate the effects with film thickness and investigate the dependence on annealing temperature are anticipated.

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Figure Captions.

Figure 1. X-ray reflectivity from carbon sample 1, nominally 400Å thick (a) before annealing and (b) after annealing at 600°C for 4 hours in a vacuum furnace. The accuracy of the data is estimated at 5%-10% and has been normalised to the incident beam intensity. The reflectivity of the annealed sample is multiplied by 100. The solid lines are simulations of the data as described in the text and represented by the parameters in Table I (before annealing) and Table II (annealed).

Figure 2. As in figure 1, but for sample 2, nominally 200Å thick (a) before annealing and (b) after annealing..

Figure 3. As in figure 1, but for sample 3, nominally 50Å thick (a) before annealing and (b) after annealing.

Table I. The parameters to the fits shown in figures 1-3(a) for the three carbon films of different thicknesses prior to annealing. The density of the silicon substrate was fixed at 2.33 gcm^{-3}.

Table II. The parameters to the fits shown in figures 1-3(b) for the carbon films after annealing.

Table I. $\rho_{Si} = 2.33$ gcm^{-3}

	Substrate	Si/C interface layer 1			Carbon layer			Contaminant layer 3			$\rho_C d_C$
	$\sigma_{Si/1}$ (Å)	ρ_1 (gcm^{-3})	d_1 (Å)	$\sigma_{1/C}$ (Å)	ρ_C (gcm^{-3})	d_C (Å)	$\sigma_{C/3}$ (Å)	ρ_3 (gcm^{-3})	d_3 (Å)	$\sigma_{3/air}$ (Å)	
Sample 1	3.7	1.64±.08	13.1±1.0	5.6±1.0	2.27±.06	366.±4	2.1±1.0	1.7	17.1	6.5	831
Sample 2	3.8	1.66	17.7	4.9	2.23	237±3	2.6	0.7	8.7	4.7	529
Sample 3	3.9	1.76	10.9	6.9	2.21	51±1	3.2	1.1	6.3	4.0	112

Table II.

	Substrate	Si/C interface layer 1			Carbon layer			Contaminant layer 3			$\rho_C d_C$
	$\sigma_{Si/1}$ (Å)	ρ_1 gcm^{-3}	d_1 (Å)	$\sigma_{1/C}$ (Å)	ρ_C gcm^{-3}	d_C (Å)	$\sigma_{C/3}$ (Å)	ρ_3 gcm^{-3}	d_3 (Å)	$\sigma_{3/air}$ (Å)	
Sample 1	2.9	1.59	14.6	3.0	2.09	399	6.2	1.3	8.9	5.1	834
Sample 2	4.0	1.47	16.4	6.6	2.05	257	1.3	0.7	7.4	0.1	527
Sample 3	2.7	1.64	14.3	4.3	2.04	54	7.5	1.0	6.9	4.6	110

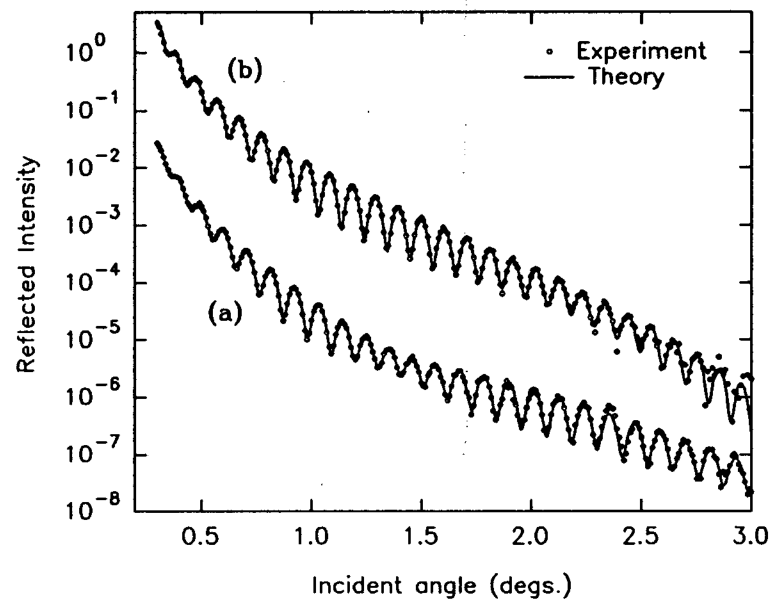

Figure 1

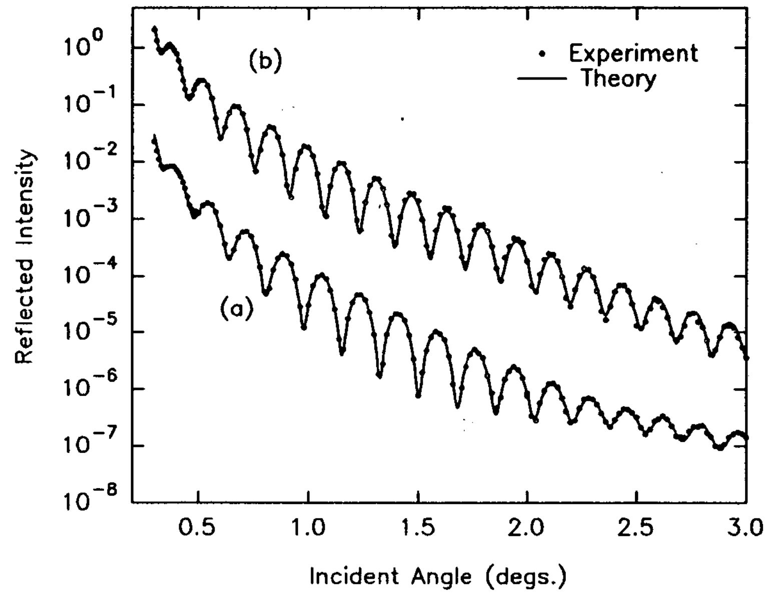

Figure 2

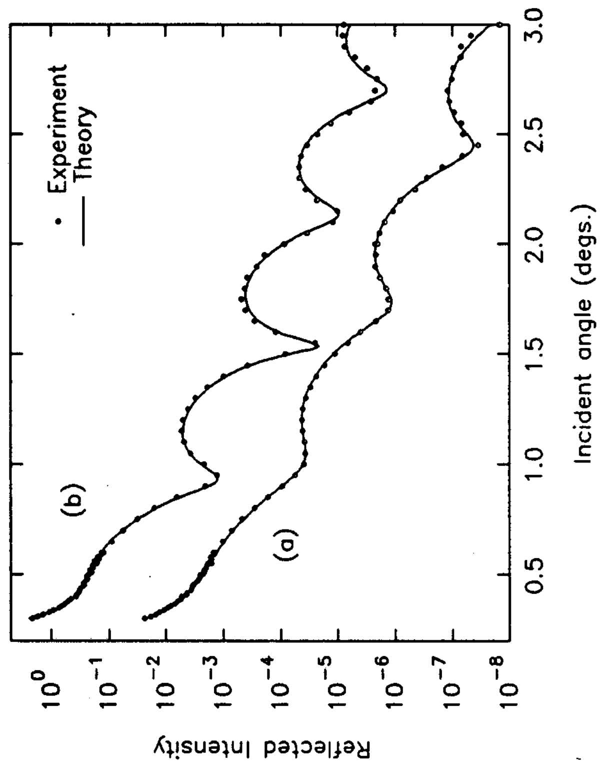

Figure 3

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