Published in final edited form as:

J Struct Biol. 2011 May ; 174(2): 420–423. doi:10.1016/j.jsb.2011.02.005.

THE SURFACE OF EVAPORATED CARBON FILMS IS AN INSULATING, HIGH-BANDGAP MATERIAL

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Abstract

The electrical conductance and the optical density of evaporated carbon films are measured as a function of the thickness of the films. The resulting data show that up to a thickness of approximately 4 nm, carbon films are optically transparent and electrically insulating. The same data also suggest that this insulating character persists near to the surface when the overall thickness is further increased. Since a support film with poor surface conductivity is undesirable for many applications in electron microscopy, we suggest that the usefulness of evaporated carbon films in electron microscopy might be further improved by doping or by other methods that improve the electrical conductivity near the surface.

Vacuum-evaporated carbon is widely used to make thin specimen-support films for electron microscopy, where it is favored due to its low atomic number (low scattering cross section), amorphous structure and excellent mechanical strength. Although evaporated carbon is a semiconductor rather than a metal, and thus its electrical conductivity decreases steeply at low temperature, its conductivity appears to be fully sufficient for use in cryo-electron microscopy. In some cases evaporated carbon is even deposited onto otherwise non-conducting materials in order to overcome problems of specimen charging (Jakubowski et al., 1989). Recently, evaporated carbon films have also been used with some success as quarter-wave plates to provide Zernike phase contrast in transmission electron microscopy (Danev et al., 2009; Nagayama, 2008).

There are nevertheless a number of indications that the surface (unlike the bulk) of evaporated carbon films is an electrical insulator, implying that a thin region at the surface may have a structure similar to one of the known, high-bandgap versions of amorphous carbon (Robertson and Oreilly, 1987; Silva, 2002). Clean carbon films, for example, although they have had no specimen applied to them, are known to often exhibit a subtle form of charging, which is sometimes referred to as the “Berriman effect” (Brink et al., 1998a; Downing et al., 2004; Glaeser and Downing, 2004). In addition, the measured phase shift for electrons passing through thin carbon films exhibits an offset that is independent of thickness, believed to be due to charging of the surface (Wanner et al., 2006). Finally, when used as a quarter-wave plate, freshly made carbon films are often prone to charging, and

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those that initially show little or no charging are certain to develop the same behavior as they age, independent of exposure to the electron beam (Danev et al., 2009).

We have previously reported that the conductance of evaporated carbon films increases linearly with thickness, but that the linear fit extrapolates to effectively zero conductance at a thickness in the range of 4 nm (Glaeser and Downing, 2004). Further investigation on our part demonstrated that the conductance of films of a given thickness was quite variable, thus making studies as a function of thickness difficult to reproduce. We thus devised a simple apparatus that allows one to produce multiple carbon films with different thicknesses in one run of the evaporator. We now report that the intercept (onset of conductance) is quite reproducible, occurring at a thickness of 5.6 ± 0.5 nm. At the same time we find that the slope can vary greatly from one evaporation-run to another. In addition, we find that a corresponding effect occurs in the optical density of the same films that are used to measure conductance, but with an intercept at a slightly smaller thickness, 4.3 ± 0.8 nm and a nearly constant slope

A rotating shutter, shown in Figure S1, similar to that described previously (Williams and Glaeser, 1972), was placed between the substrate and the carbon arc in a vacuum evaporator in order to simultaneously produce four films under identical conditions, but with different thicknesses. In order to avoid complications associated with the use of a quartz monitor to measure carbon-film thicknesses (e.g. a temperature change due to radiant heating of the detector), the thickness values for each of the carbon films were measured by picking up fragments on a continuous carbon film and measuring the length of the shadow cast when nichrome alloy was evaporated at a shallow angle to the surface, as is shown in Figure S2. We are confident that the results presented here will be easily reproduced by other investigators as long as measurements are made on films of different thickness that are produced in a single evaporation run.

The conductance of evaporated carbon films increases linearly with thickness, but only for films thicker than ~5–6 nm

The thin carbon films used to measure both the conductance (and the optical density) as a function of thickness were deposited onto cleaned glass “half” cover slips (Gold Seal 12×24 mm). After the carbon was deposited, a 3 mm strip in the center was masked by a small piece of plastic, and a thick layer of gold was evaporated onto the remaining, exposed carbon in order to create an area of good electrical contact at the ends of the coverslips. An example of the final product is shown in Figure S3.

A Fluke 87 Ohm meter was used to measure the resistance, R , between the gold pads. The Fluke meter has a maximum resistance measurement of 300MΩ, however, and thus the resistance of the thinnest carbon films was confirmed by placing a voltage across the film (1 volt) and measuring the current with an Advantest R8240 pico-ammeter. The conductance, G , was calculated as the reciprocal of the resistance.

If the conductance of thin carbon films did not show any surface effects, then the measured conductance would increase linearly with thickness, and the straight line would extrapolate to the origin. As is shown in Figure 1, the conductance of evaporated carbon films does indeed increase linearly with thickness, but the straight line extrapolates to zero conductance at a thickness of 5.6 ± 0.5 nm. The same sort of linear, but not proportional increase was seen when the conductance of an evaporated carbon film was measured continuously during evaporation, and a quartz monitor was used to estimate the amount of evaporated carbon (Glaeser and Downing, 2004). As indicated above, however, the absolute thickness of the carbon film at which conductance begins to increase is more difficult to measure with a

quartz monitor due to the confounding thermal effect when the monitor is exposed to the hot carbon source. Even so, the presence of the same effect for measurements made in vacuum, in real time, minimizes the chance that adsorbed contaminants are responsible for the observed effect.

This behavior suggests that the conductivity of the bulk (the interior) of a given set of evaporated carbon films does not depend upon the thickness, but that the region that is close to the surface has a much lower conductivity than that of the bulk. The data in Figure 1 also show that the slope of the curves is quite different for sets of carbon films that were evaporated in different runs, even though the intercepts are very similar. This result implies that the bulk conductivity of evaporated carbon films is quite sensitive to the exact conditions under which the evaporation was performed. Although we have no data that could explain the variability in the bulk conductivity, it is not difficult to suggest factors that could account for the variability such as the rate of condensation of carbon or the pressure (and even the composition) of residual gasses in the vacuum at the time of evaporation.

The optical density of evaporated carbon films increases linearly with thickness, but only for films thicker than ~4 nm

The optical density values of the various carbon films were measured by scanning the carbon-coated glass substrates, described above, with the same microdensitometer (Nikon Coolsan 8000) that we routinely use to digitize photographic films. A clean coverslip was used as the zero-OD reference to compensate for the reflectance of the glass slide, and the region covered with one of the gold pads was used as a reference for zero transmittance. It is well known, of course, that carbon films that are evaporated at high vacuum absorb light at all wavelengths in the visible, and some investigators use the optical density of their carbon films to estimate the thickness of the films. As is shown in Figure 2, the optical density increases linearly with the thickness of the carbon film. Once again, however, the straight line extrapolates to zero at a finite thickness rather than at the origin. In this case the intercept occurs at a thickness of $4.3 \pm 0.8\text{nm}$, which is slightly less than the intercept measured for the electrical conductance. This behavior suggests that the molar extinction coefficient of the bulk (the interior) of the evaporated carbon film does not depend upon the thickness, but that the region that is close to the surface has a much lower molar extinction coefficient than that of the bulk. In addition, the data show that the slopes of the various OD versus thickness curves are all very similar. This result implies that the molar extinction coefficient for the bulk phase of evaporated carbon films is relatively independent of the parameters that can cause the electrical conductance to be quite variable.

The occurrence of non-zero intercepts for both the optical density and the electrical conductance suggests that the region near the surfaces of evaporated carbon films may be a high-bandgap, insulating material

The literature on amorphous carbon recognizes that the optical and electrical properties of such materials depend strongly on whether the chemical bonding is predominantly trigonal (sp^2 , or graphite-like) or tetrahedral (sp^3 , or diamond-like) (Robertson and O'Reilly, 1987; Silva, 2002). Extensive trigonal (sp^2) bonding naturally results in highly delocalized (conjugated double-bond, i.e. π -electron) electronic states for which there is a relatively small gap between the ground state and the first excited state. As a result, such materials absorb light intensely across the entire visible spectrum, as does graphite, for example. In addition, the delocalized nature of the excited-state (i.e. π^*) electron wave functions provides for good electrical conductivity of the material. Predominantly tetrahedral (sp^3) bonding, on the other hand, results in electronic states that are localized to individual

carbon-carbon bonds, for which there is a rather large energy gap between the ground state and the first excited state. As a result, such materials are transparent over the entire spectrum of visible light, as is diamond. In addition, such materials are electrical insulators.

The fact that evaporated carbon films thinner than ~4 nm are optically transparent implies that the band gap between the (filled) ground-state and the (empty) excited state wave functions is more than 2.5 eV, and that there are few impurity and/or defect states whose energies lie within the gap. It thus is clear that the very thin, optically transparent films must have a very low electrical conductivity, i.e. that they would be electrical insulators.

It is also clear that carbon films with increasing thickness contain increasing amounts of material with a much smaller band gap, thus allowing the optical density to increase across the full spectrum of visible light. What is not known *a priori*, however, is whether regions with delocalized π^* wave functions are electrically connected to one another, or whether they are electrically isolated from one another as they are for dye molecules in a non-conducting matrix. The fact that the onset of electrical conductance occurs slightly later than does the onset of optical density suggests that the initial regions where delocalized π^* wave functions exist are not, in fact, electrically connected, but that they very soon do become connected as the thickness increases. The additional fact that the resulting conductivity of the low band-gap material nevertheless varies considerably from one set of evaporated carbon films to another suggests, however, that the extent to which the delocalized π^* wave functions are electrically connected can vary with the conditions under which the evaporated carbon films are grown.

It is hard to understand, however, why the chemical bonding in a thin film of evaporated carbon would initially be tetrahedral (diamond-like), but at a certain thickness it would switch over to being trigonal (graphitic). In addition, it is puzzling why even the thinnest carbon films would have a diamond-like bonding configuration, since graphite is a lower-energy material than is diamond.

One consideration that may be important is that carbon atoms on the surface can form covalent bonds to other carbon atoms on the interior, but they cannot form covalent bonds to the substrate (or to vacuum). As a result, the lowest-energy bonding configuration for atoms on the surface is not necessarily the same as that in the bulk. The preferred bonding configuration for the surface atoms would furthermore persist for some distance into the bulk, before it would become favorable for the thermodynamically more stable bonding configuration to take over. We thus suggest that one scenario that is consistent with the data is that the covalent bonding configuration is predominantly diamond-like for the thinnest carbon films, but that reconstruction of the bonding configuration occurs in the interior as more atoms are added to the surface. This (bulk-reconstruction) model further suggests that tetrahedrally-bonded layers may be present on both surfaces of evaporated carbon films that are thicker than ~5–6 nm, and thus the thickness of each such surface layer would be only ~2.5–3 nm.

Irradiating very thin carbon films with 80 keV electrons, under conditions similar to those recommended by Miyazawa et al. (Miyazawa et al., 1999), did not produce a measurable increase in conductance. Other, relatively minor discrepancies between our experimental results and those reported by Miyazawa are described in the supporting material.

Recognizing that the surface and the bulk of evaporated carbon films may have different chemical-bonding and electrical properties has important significance for further exploitation of such films

Thin carbon films are remarkably effective in preventing charging effects for specimens that are used in electron microscopy (Brink et al., 1998b; Jakubowski et al., 1989). In our own experience, even a carbon film as thin as 5 nm is perfectly effective in preventing obvious “charging” effects that would otherwise be seen, for example when using a non-conducting specimen such as a thin formvar film or a thin plastic section. It is thus necessary to reconcile the operational effect that even very thin carbon films are effective in preventing charging, with the results presented here, which state that 5-nm thick carbon films have little electrical conductivity. One possible explanation may be that even very thin carbon films (and the surfaces of thicker carbon films) can show a high level of radiation-induced conductivity – for background, see (Ehrenberg and Gibbons, 1981). It is entirely possible for this to be the case, since ionizing radiation deposits sufficient energy to easily excite electrons into conduction bands, even in high-bandgap materials.

Although carbon films are effective in preventing effects that one normally attributes to charging, as we stated above, they generally exhibit a more subtle (lower level of) charging that is commonly referred to as the Berriman effect (Brink et al., 1998a; Downing et al., 2004). This more subtle form of charging requires that there be either non-conducting sample materials or a “native insulating layer” on the surface of a conducting film (Glaeser and Downing, 2004). In such a situation, charging of the insulating layer produces only a dipole layer rather than the spot of uncompensated charge that is normally imagined when one discusses charging.

Even this more subtle form of charging could contribute to beam-induced specimen movement, through the mechanical stress associated with Coulombic repulsion between immobile charges on the surface. In addition, surface charging (i.e. the Berriman-effect type of charging) is likely to be problematic whenever it occurs on thin carbon films that are used as quarter-wave plates for Zernike phase contrast in electron microscopy.

Evidence that the surface of evaporated carbon films may be an insulator rather than a semiconductor (like the bulk-phase of such films) now suggests that the properties of evaporated carbon films might be improved by finding ways to improve the electrical conductivity of the surface. Doping the surface layer with gadolinium (Zeng et al., 2007) or other materials is one approach that could be successful. Less specifically, one can imagine that it may be possible to chemically modify the surface of evaporated carbon films such that the chemical bonding requirements of atoms at the surface can be satisfied in a way that is similar to the trigonal (graphitic) bonding that is preferred in the bulk.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported in part by the US Department of Energy under Contract DE-AC02-05CH11231 and by NIH grant P01 GM51487.

References

- Brink J, Sherman MB, Berriman J, Chiu W. Evaluation of charging on macromolecules in electron cryomicroscopy. *Ultramicroscopy*. 1998a; 72:41–52. [PubMed: 9561796]
- Brink J, Gross H, Tittmann P, Sherman MB, Chiu W. Reduction of charging in protein electron cryomicroscopy. *Journal of Microscopy-Oxford*. 1998b; 191:67–73.
- Danev R, Glaeser RM, Nagayama K. Practical factors affecting the performance of a thin-film phase plate for transmission electron microscopy. *Ultramicroscopy*. 2009; 109:312–325. [PubMed: 19157711]
- Downing KH, McCartney MR, Glaeser RM. Experimental characterization and mitigation of specimen charging on thin films with one conducting layer, p. 2004; 783–789:783–789.
- Ehrenberg, W.; Gibbons, DJ. Electron bombardment induced conductivity and its applications. Academic Press; London: 1981.
- Glaeser RM, Downing KH. Specimen charging on thin films with one conducting layer: Discussion of physical principles. *Microscopy and Microanalysis*. 2004; 10:790–796. [PubMed: 19780321]
- Jakubowski U, Baumeister W, Glaeser RM. Evaporated Carbon Stabilizes Thin, Frozen-Hydrated Specimens. *Ultramicroscopy*. 1989; 31:351–356.
- Miyazawa A, Fujiyoshi Y, Stowell M, Unwin N. Nicotinic acetylcholine receptor at 4.6 angstrom resolution: Transverse tunnels in the channel wall. *Journal of Molecular Biology*. 1999; 288:765–786. [PubMed: 10329178]
- Nagayama K. Development of phase plates for electron microscopes and their biological application. *European Biophysics Journal with Biophysics Letters*. 2008; 37:345–358. [PubMed: 18259741]
- Robertson J, Oreilly EP. ELECTRONIC AND ATOMIC-STRUCTURE OF AMORPHOUS-CARBON. *Physical Review B*. 1987; 35:2946–2957.
- Silva, R. Properties of Amorphous Carbon. Institution of Engineering & Technology Books International, Incorporated [Distributor]; Stevenage; Herndon: 2002.
- Wanner M, Bach D, Gerthsen D, Werner R, Tesche B. Electron holography of thin amorphous carbon films: Measurement of the mean inner potential and a thickness-independent phase shift. *Ultramicroscopy*. 2006; 106:341–345. [PubMed: 16343774]
- Williams RC, Glaeser RM. ULTRATHIN CARBON SUPPORT FILMS FOR ELECTRON-MICROSCOPY. *Science*. 1972; 175:1000. [PubMed: 4333169]
- Zeng L, Helgren E, Hellman F, Islam R, Smith DJ, Ager JW. Microstructure, magnetotransport, and magnetic properties of Gd-doped amorphous carbon. *Physical Review B*. 2007:75.

Figure 1.

Electrical conductance of evaporated carbon films of various thicknesses. Four films of different thickness were prepared during a single evaporation run. Data are shown for four such experiments. For each batch of carbon films the conductance is extremely low until the carbon film reaches a thickness of 5 to 6 nm, after which the conductance increases linearly with thickness. Although the slope of the increase is variable from one batch to another, the intercept is virtually identical for all four experiments.

Figure 2.

Optical density of evaporated carbon films of various thicknesses. These measurements were made on the same specimens for which the conductance is reported in Figure 1. The optical density increases linearly with thickness, but with an intercept of zero optical density at a thickness of ~4 nm.