Layer-by-Layer Assembly of Ultrathin Composite Films from Micron-Sized Graphite Oxide Sheets and Polycations

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Unilamellar colloids of graphite oxide (GO) were prepared from natural graphite and were grown as monolayer and multilayer thin films on cationic surfaces by electrostatic self-assembly. The multilayer films were grown by alternate adsorption of anionic GO sheets and cationic poly(allylamine hydrochloride) (PAH). The monolayer films consisted of 11−14 Å thick GO sheets, with lateral dimensions between 150 nm and 9 μm. Silicon substrates primed with amine monolayers gave partial GO monolayers, but surfaces primed with $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ ions gave densely tiled films that covered approximately 90% of the surface. When alkaline GO colloids were used, the monolayer assembly process selected the largest sheets (from 900 nm to 9 μm) from the suspension. In this case, many of the flexible sheets appeared folded in AFM images. Multilayer $(GO/PAH)_n$ films were invariably thicker than expected from the individual thicknesses of the sheets and the polymer monolayers, and this behavior is also attributed to folding of the sheets. Multilayer $(GO/PAH)_n$ and $(GO/polyaniline)_n$ films grown between indium−tin oxide and Pt electrodes show diodelike behavior, and higher currents are observed with the conductive polyaniline-containing films. The resisitivity of these films is decreased, as expected, by partial reduction of GO to carbon.

Introduction

The assembly of composite thin films from lamellar inorganic particles and organic macromolecules is an inexpensive and versatile route to functional nanometer-scale structures.[1] These films are grown by a wet chemical, layer-by-layer adsorption method, which is similar to that developed earlier by Decher and co-workers for organic polyelectrolytes.[2] The addition of inorganic components offers the possibility of added optical, electronic, magnetic, mechanical, and thermal properties that may be difficult to achieve by using organic polymers alone. Additionally, the continuous inorganic sheets provide a barrier to interpenetration of sequentially deposited polymer or nanoparticle layers, a feature that can be important in thin films intended to act as current rectifiers, photodiodes, or Coulomb blockade devices. Several electronic and photonic applications along these lines have established the utility of this method.[3]

The layer-by-layer assembly method relies on the exfoliation of solids to produce colloids of sheets, which typically have nanometer thicknesses and lateral dimensions of tens of nanometers to microns. Exfoliation procedures based on ion exchange and redox reactions have been developed for a variety of lamellar solids.[4] Thus, multilayer inorganic/organic films have been grown from lamellar metal phosphates, titanates, niobates,[5] silicates,[1b] and metal chalcogenides,[6] compounds which in bulk form possess transport properties ranging from insulating to semimetallic. Recently, Fendler and co-workers have shown that such films can also be

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grown from graphite oxide (GO),[7] which can subsequently be reduced electrochemically to make electronically conducting graphitic films. In their work, GO nanoparticles were prepared from synthetic graphite. They noted that the multilayer films consisted of incompletely exfoliated platelets that were tens of nanometers in their lateral dimensions. In this paper, we revisit the assembly of GO/polycation thin films, using GO prepared from natural crystals. We show that exfoliated GO derived from these crystals is a mechanically robust material that deposits conformally on cationic surfaces as micron-sized, nanometer-thick sheets.

Graphite oxide is a pseudo-two-dimensional solid in bulk form, with strong covalent bonding within the layers. Weak interlayer contacts are made by hydrogen bonds between intercalated water molecules.[8−11] The carbon sheets in GO contain embedded hydroxyl and carbonyl groups, as well as carboxyl groups situated mainly at the edges of the sheets.[8,9,12] While there is no consensus as to the precise structure of GO layers, different structural models,[9a,b,10] which correspond to an ideal formula of $C_8O_2(OH)_2$, have been advanced. A recent study of the structure of GO argues from ^{13}C and ^1H NMR evidence for the presence of epoxy groups.[13] Nakajima and co-workers have proposed that the carbon layers in GO are linked together in pairs by sp^3 C−C bonds perpendicular to the sheets.[10] According to Klinowski et al.,[13] the carbon layers in GO contain two kinds of domains, aromatic regions with unoxidized benzene rings and aliphatic regions with six-membered carbon rings. The relative size of the domains, which are randomly distributed, depends on the degree of oxidation. In both models, the hydroxyl groups project above and below the carbon grid. The phenolic hydroxyl groups are acidic and, together with the carboxyl groups, are responsible for the negative charge on the GO sheets in aqueous suspensions.[9,13] The surface charge density of colloidal GO particles (degree of oxidation 85%) was measured by Fendler and co-workers as 0.4 per 100 Å^2.[7]

The GO interlayer distance is not constant and depends strongly on the GO:H_2O ratio.[8−10,15] In very dilute aqueous suspensions, the interlayer distance is large, so interaction between the layers is sufficiently weak that exfoliation occurs.[8] Our previous research showed that the number of layers in the GO colloidal particles can be controlled by the dilution of the suspensions.[16,17] The adsorption capacity for Cu(II) ions, which was for both aqueous suspensions[16] and thin films deposited from these suspensions on powder supports (ZnO, Al_2O_3, fumed SiO_2),[17] increased with decreasing GO concentration in the starting suspension. For example, the adsorption capacity of GO films on SiO_2 increased by a factor of 2.4 when the GO concentration in the starting suspension was decreased from 1.0 to 0.3 g/L. This result shows that more complete exfoliation provides increased access to the GO functional groups. For samples prepared from the colloids with GO concentrations of 0.02−0.3 g/L, the maximum adsorption capacity, 22−24 mmol/g, was obtained. This value is close to the total quantity of oxygen-containing groups in GO (25 mmol/g[9]) and gives indirect evidence that dilute GO colloids are exfoliated as monolayers.

We report here a detailed study of the preparation and characterization of GO/polycation films grown on planar Si and Al_2O_3/Al supports. Using atomic force microscopy (AFM), ellipsometry, and electrical measurements, the following questions have been addressed:

What does the first layer of the sheets adsorbed on a substrate look like microscopically?

Can we affect the quality of mono- and multilayer films by varying the conditions of their deposition and the chemical composition of the substrate surface?

What are the electronic properties of GO/polycation films, and how are they influenced by the nature of the polycation?

Experimental Section

Materials. GO was synthesized from natural graphite powder (325 mesh, GAK-2, Ukraine) by the method of Hummers and Offeman.[18] It was found that, prior to the GO preparation according to ref 18, an additional graphite oxidation procedure was needed. Otherwise, incompletely oxidized graphite-core/GO-shell particles were always observed in the final product. The graphite powder (20 g) was put into an 80 °C solution of concentrated H_2SO_4 (30 mL), $K_2S_2O_8$ (10 g), and P_2O_5 (10 g). The resultant dark blue mixture was thermally isolated and allowed to cool to room temperature over a period of 6 h. The mixture was then carefully diluted with distilled water, filtered, and washed on the filter until the rinse water pH became neutral. The product was dried in air at ambient temperature overnight. This preoxidized graphite was then subjected to oxidation by Hummers' method. The oxidized graphite powder (20 g) was put into cold (0 °C) concentrated H_2SO_4 (460 mL). $KMnO_4$ (60 g) was added gradually with stirring and cooling, so that the temperature of the mixture was not allowed to reach 20 °C. The mixture was then stirred at 35 °C for 2 h, and distilled water (920 mL) was added. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (2.8 L) and 30% H_2O_2 solution (50 mL), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with 1:10 HCl solution (5 L) in order to remove metal ions. The GO product was suspended in distilled water to give a viscous, brown, 2% dispersion, which was subjected to dialysis to completely remove metal ions and acids. The resulting 0.5% w/v GO dispersion, which is stable for a period of years, was used to prepare exfoliated GO.

Exfoliation was achieved by dilution of the 0.5% GO dispersion (1 mL) with deionized water (24 mL), followed by 15 min sonication. The resulting homogeneous yellow-brown sol, which contained 0.2 g/L GO, was stable for a period of months and was used for film preparation.

An aqueous solution (0.01 M) of poly(allylamine hydrochloride), PAH, (Aldrich, MW = 50 000−65 000) was adjusted to pH 7 with NH_3 and was used for growth of polycation layers.

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An aqueous solution of doped polyaniline (PAN) was made from a saturated solution of the emeraldine base form in dimethylformamide. A 3 mL portion of this solution was slowly added with stirring to 26 mL of water, which had been acidified to pH 3.5 with aqueous HCl. The pH of the final PAN solution was then adjusted to 2.5 by addition of aqueous HCl. The aluminum Keggin ion $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ was prepared trom $Al_{13}O_4(OH)_{25}(H_2O)_{11}(SO_4)_3{\cdot}x(H_2O)$, which was available from a previous study.[5] Briefly, 0.102 g of the sulfate salt was added to a solution of 0.042 g of $BaCl_2$ in 200 mL of water and stirred overnight. The resulting 0.3 mM solution of the chloride salt of the aluminum Keggin ion was filtered using a 0.2 μm filter.

Polished (100) Si wafers were sonicated in CCl_4 for 15 min and then rinsed with 2-propanol and water. Their surface was then hydroxylated by 30 min sonication in "piranha" solution (4:1 concentrated H_2SO_4:30% H_2O_2) (**CAUTION**: piranha solution reacts violently with organic compounds!) and was rinsed sequentially with water, methanol, and 1:1 methanol/toluene before the surface derivitization steps began.

Aluminum foil, Al-coated glass, both bearing a native oxide, and ITO glass were cleaned by washing with hexane for 15 min prior to GO adsorption.

Multilayer GO/PAH Film Growth. Hydroxylated silicon wafers were primed with one of three different types of cationic monolayers in order to initiate the growth of the GO films. This was achieved either by (1) reacting with 4-((dimethylmethoxy)silyl)butylamine (15 h treatment with a 5% toluene solution under dry Ar, over KOH at ambient temperature) or by (2) adsorbing a monolayer of aluminum Keggin ions (5 min adsorption from aqueous solution of the chloride salt at 80 °C[19]) or by (3) adsorbing PAH (15 min adsorption from a 0.01 M aqueous solution at pH 7 and ambient temperature). The primed Si substrates (1, 2, and 3) are designated hereafter as $Si(NH_2)$, Si(OH)/Al-Kg, and Si(OH)/PAH, respectively.

The primed substrates were immersed in an aqueous (pH 5) or aqueous ammonia (pH 9) GO sol (0.2 g/L) for 15 min and then rinsed with deionized water and dried in flowing Ar. The samples were then immersed in aqueous PAH solutions for 15 min, rinsed with deionized water, and dried in flowing Ar. Multilayer GO/PAH films were grown by repeating these adsorption cycles. Preliminary experiments had shown that the thickness of a deposited layer (estimated by ellipsometry) does not depend on the substrate/solution contact time in the range from 2 min to 2 h. For electronic measurements, multilayer $(GO/PAH)_{14}$ and $(GO/PAN)_{30}$ films were grown on ITO in similar adsorption cycles. For comparison purposes, a GO colloid film (ca. 90 nm thick) was prepared by dip-coating the ITO/glass in the GO colloidal dispersion.

Characterization. Atomic force microscopy (AFM) images of the layers deposited on Si substrates were obtained with a Digital Instruments Nanoscope IIIa in tapping mode, using a 3045 JVW piezo tube scanner. The 125 μm etched Si cantilevers had a resonant frequency between 250 and 325 kHz, and the oscillation frequency for scanning was set to ~0.1–3 kHz below resonance. Typical images were obtained with line scan rates of 2 Hz while 256 × 256 pixel samples were collected.

Ellipsometric measurements were made with a Gaertner model L2W26D ellipsometer. An analyzing wavelength of 632 nm was used, because GO absorbs minimally at this wavelength. The incident angle was 70° and the polarizer was set at 45°. Ellipsometric parameters were measured following each GO or PAH adsorption step. Si substrates were dried in an Ar stream before each measurement. The film thickness of the GO/PAH multilayers was calculated using the Si refractive indices, $n_s = 3.875$ and $k_s = -0.018$, determined from a blank sample. The refractive index of GO/PAH films was estimated as $n_f = 1.540$, $k_f = 0$.

Transmission electron microscope (TEM) images were obtained with a JEOL 1200 EXII microscope at 120 kV accelerating voltage. Samples were prepared by immersing a copper grid in the GO sol and drying in air.

The elemental composition of GO was determined by using a home-built mass spectrometer with laser probe (LMS). The diameter of the crater for single laser impulse was 0.42–0.48 mm, and the depth was 1 μm. IR spectra were recorded using a Perkin-Elmer 325 instrument. XPS spectra were obtained using a Kratos Series 800 spectrometer with $h\nu$=1253.6 eV and an analyzing window of 4 × 6 mm^2. The accuracy of the measured core level binding energies (E_b) was 0.1 eV. For LMS, IR, and XPS experiments, GO samples were prepared as films by drying a droplet of the sol in air at ambient temperature. X-ray powder diffraction (XRD) patterns were recorded with a DRON-1 instrument using Cu Kα radiation. Prior to the measurement, the GO sample was dried in a vacuum over P_2O_5 for 24 h.

Electrical measurements of films deposited on ITO glass were carried out using top Pt electrode contacts that were 10 μm in diameter and mechanically pressed into the film, using a home-built parametric analyzer. The sensitivity of current measurements was 0.01 nA. All measurements were carried out in air at ambient temperature. The turn-on potential for all thin film devices studied was taken as the potential at which a current of 1.0 nA was observed. In regions where current was more than 3 nA, every step of voltage increase (typically 0.1 mV in both the forward and reversed directions) was followed by repeating the measurement cycle to ensure the reproducibility of the current measured at the lower voltage. Measurements were considered irreversible (i.e., a permanent change to a more conductive state occurred) when the current recorded the second time at the lower voltage was noticeably higher than that measured in the previous cycle.

Results and Discussion

Characterization of the GO Colloid. The XRD pattern of GO prepared by preoxidation with persulfate followed by oxidation with permanganate reveals a sharp 002 reflection at $2\theta = 12.80°$, which corresponds to a c-axis spacing of 6.91 Å This value falls within the range of 6.3–7.7 Å reported in the literature[9a,10,20,21] for GO prepared from natural graphite according to Hummers' method.[18] No 002 diffraction peak from unreacted graphite ($d = 3.35$ Å) is observable in the XRD pattern.

The IR spectrum of GO prepared by this method is essentially identical to that reported in the literature.[9a,12,21] A band at 3420 cm^{-1} and a broad band centered around 3220 cm^{-1} are attributed to O–H stretching vibrations of the C–OH groups and water, respectively; a band at 1730 cm^{-1} is assigned to C=O stretching vibrations of the carbonyl and carboxyl groups. Bands at 1365, 1425, and 1615 cm^{-1} are assigned to the O–H deformations of C–OH groups and water, respectively. A band at 1080 cm^{-1} is due to C–O stretching vibrations.

Deconvolution of the C1s peak in the XPS spectrum shows the presence of four types of carbon bonds: C–C (284.8 eV), C–O (286.2 eV), C=O (287.7 eV), and O–C=O (288.5 eV). By integrating the area of the deconvolution peaks, the following approximate percentages were obtained: C–C, 49.5; C–O, 31.4; C=O, 9.1; O–C=O, 2.9.

The LMS spectrum of GO prepared by this method gave the following atomic composition (wt %): H, 2.3; C, 45.2; O, 46.5; P, 3.3; K, 2.7; C:O ratio = 1.3. The same or nearly the same C:O ratio has been found previously for GO samples prepared from natural graphite.[21,22] It is generally accepted that the conversion of graphite to

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Figure 1. Transmission electron micrograph of colloidal graphite oxide particles.

GO is complete when the C:O ratio becomes 2.0. The observed ratio C:O:H = 4:3.1:2.5 is richer in O and H than that calculated for $C_8O_2(OH)_2$: 4:2:1; this can be explained by the presence of intercalated/adsorbed water and carboxyl groups, as shown by IR and XPS. It should be noted that the ideal formulation does not take into account the presence of carboxyl groups, which are mainly situated on the edges of the sheets,[8] or intercalated water, some amount of which is probably an integral part of the GO structure.[3] Allowing that 2.9% of the carbon atoms are present as carboxyl groups (from XPS) and assuming that the potassium ions are incorporated by ion-exchange, we calculate a formula of $C_{3.77}O_{2.05}H_{0.92}K_{0.07}\cdot 0.73H_2O$, or $C_8O_{2.25}(OH)_{1.95}(OK)_{0.15}\cdot 1.55H_2O$, which gives a C:O:H ratio of 4:2.95:2.5. The remaining oxygen (2.05 wt %) is most probably bound to phosphorus, an impurity introduced by the graphite preoxidation step.

TEM images of the GO sol (Figure 1) reveal flexible, wrinkled sheets of different lateral sizes ranging from hundreds to thousands of nanometers. Flexible GO particles were also observed by Hennig and Carr.[14,20] No graphite particles are observed in these images.

AFM Images of the First Adsorbed GO Layer. *Si Substrates.* AFM images (Figure 2a–c) of the GO films deposited in one adsorption cycle from aqueous solution show surface coverages of about 30% for $Si(NH_2)$, 85% for Si(OH)/PAH, and 90% for Si(OH)/Al-Kg substrates. The main features are 150–900-nm-wide islands, whose size is close to that determined by TEM for the GO sheets. In some cases, corrugations and the turned-in edges of the sheets are seen. For the PAH-primed Si substrate, the average roughness of the sheet-covered part of the surface is 4.5 Å By comparison, the roughness of the Si(OH)/PAH substrate was 6.2-Å, indicating slight smoothing of the surface by the GO monolayer. The height of the islands on $Si(NH_2)$ and Si(OH)/PAH, 10.6–14.1 Å, and the average roughness of their surface, 3.9–4.5 Å, are consistent with exposure of GO basal planes covered by adsorbed H_2O.[8–10] Ellipsometric measurements gave 11 and 14 Å thicknesses for GO monolayers on $Si(NH_2)$ and Si(OH)/PAH. Considering that the thickess of the priming layer is about 7 Å, and that the GO sheets cover only part of the surface, these results are in reasonable agreement with the island heights measured by AFM.

According to Nakajima's structural model,[10] the thickness of a GO monolayer depends on the content of hydroxyl groups on its basal planes and can reach 8.2 Å for the completely hydroxylated monolayer. Assuming the presence of completely hydroxylated GO carbon layers in very dilute colloids, one can take the thickness of a GO monolayer as 8.2 Å. By comparing this value with the height of the islands in Figure 2, one can conclude that the islands consist of a single GO sheet covered by a layer of adsorbed water molecules. The thickness of doubled GO layers can be estimated from the thickness of two GO monolayers, 2 × 8.2 Å, plus the distance between the layers, which is determined by the thickness of the layer of weakly bound mobile water molecules.[11,13] This interlayer distance can be estimated at about 3 Å, from the repeat distance along the *c*-axis of well-hydrated GO samples, I_c =11 Å,[9,14] minus the thickness of a GO monolayer, 8.2 Å. This means the thickness of doubled GO layers should be about 20 Å or more, if water adsorbed onto the top basal plane is considered. This value is significantly greater than the height of adsorbed islands (10.6–14.1 Å). The height, 20.1 Å, of the GO islands adsorbed onto the Al-Keggin-primed Si surface (Figure 2b) is roughly consistent with the thickness of the Al-Keggin anchoring layer (7 Å[23]) and a monolayer of GO sheets covered by adsorbed H_2O (10.6–14.1 Å).

An AFM image of the first GO layer adsorbed from an aqueous ammonia suspension (pH 9) onto a $Si(NH_2)$ substrate is shown in Figure 2d. In this case, the adsorption process selects much larger sheets (900–9000 nm) which cover about 60–65% area of the surface. The dissociation of the GO hydroxyl groups (situated mainly on the basal planes) occurs around pH 9 and significantly increases the negative charge density on the GO sheets. The increased attraction of the sheets for the cationic surface results in higher coverage than that observed at lower pH. This interaction is apparently more effective for the larger sheets, which can bridge over neutral regions of the incompletely primed surface. Previous studies have shown that the amine priming layer does not completely cover the surface, and that it is only partially protonated at pH 9.[5] The average roughness of the sheets on the surface is 4.4 Å. The height of the sheets, which are corrugated and sometimes have turned-in edges, is in the range of 19–23 Å. The increased thickness may be due to a hydrated layer of charge-compensating NH_4^+ ions, which cover the basal plane surface. The adsorption of a bilayer of sheets

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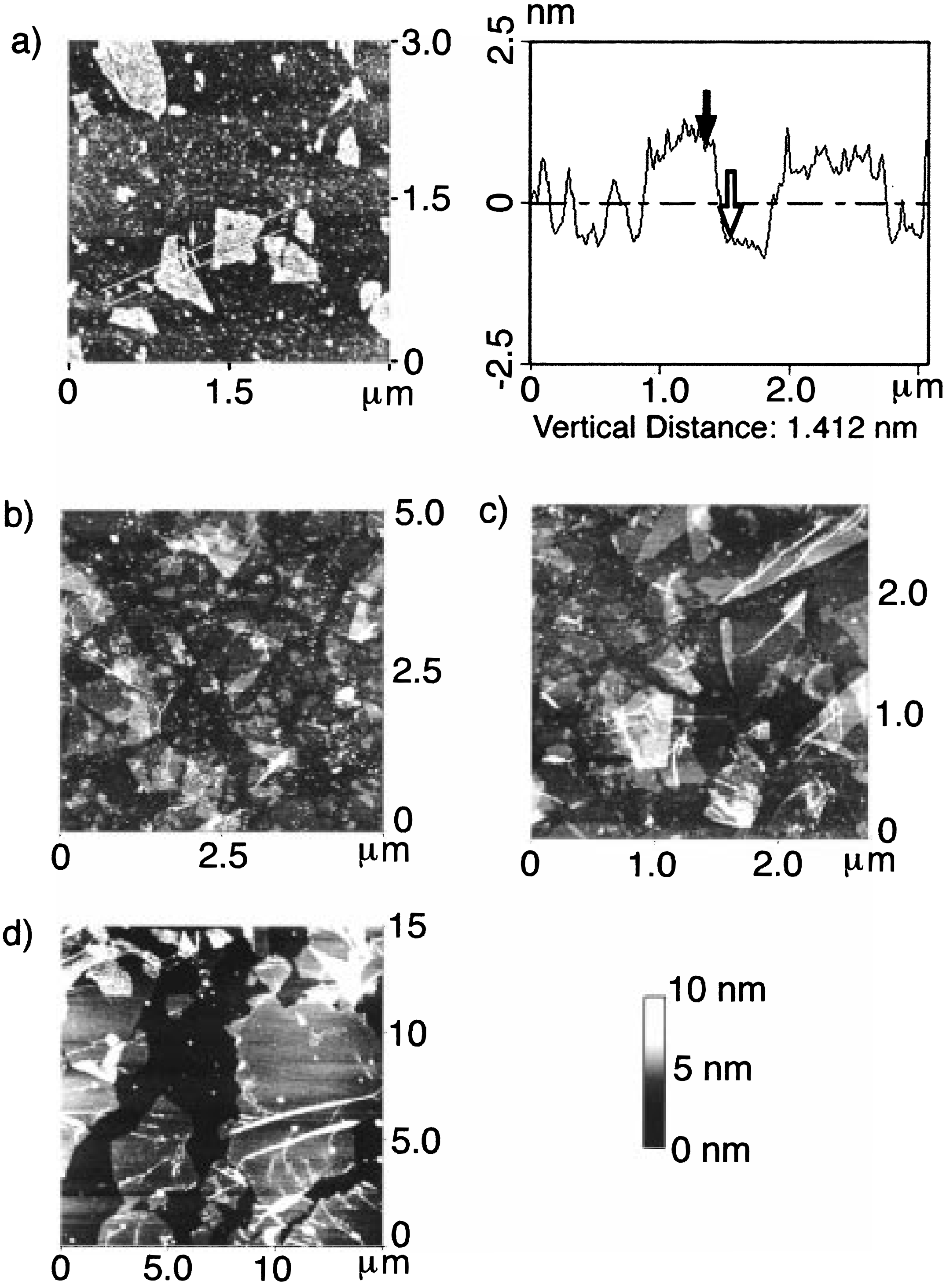

Figure 2. Tapping-mode AFM images of the first graphite oxide layer deposited from aqueous and aqueous ammonia sols on primed Si substrates: (a) Si(NH_2), GO sol pH 5, with the linescan showing the apparent height of sheet (14 Å) above the background; (b) Si(OH)/Al-Kg, GO sol pH 5; (c) Si(OH)/PAH, GO sol pH 5; and (d) Si(NH_2), GO sol pH 9.

seems unlikely, since in basic media the exfoliation of GO occurs more readily.[8]

Al_2O_3/Al Substrates. AFM images of the first GO layer grown on Al-coated glass (Figure 3a) and aluminum foil (not shown) resemble those of the substrates, except that corrugations similar to those seen in the TEM image of GO and AFM images of the GO/Si have appeared. Because both Al_2O_3/Al substrates are very rough and because the flexible GO sheets conform to the surface, it is not possible to determine the lateral and vertical dimensions of the sheets. However, the average roughness of the brighter area in the image, which is presumed to have an adsorbed GO sheet, is 2.7 nm. By comparison, the substrate roughness is 3.5-nm, again indicating a slight smoothing of the surface by the GO sheets.

Characterization of GO/PAH Multilayers.

Ellipsometry. Figure 4 shows plots of film thickness, determined by ellipsometry, versus the number of adsorption cycles for GO/PAH multilayer films. The films were grown on Si(NH_2), Si(OH)/PAH, and Si(OH)/Al-Kg substrates. The linearity of the film thickness

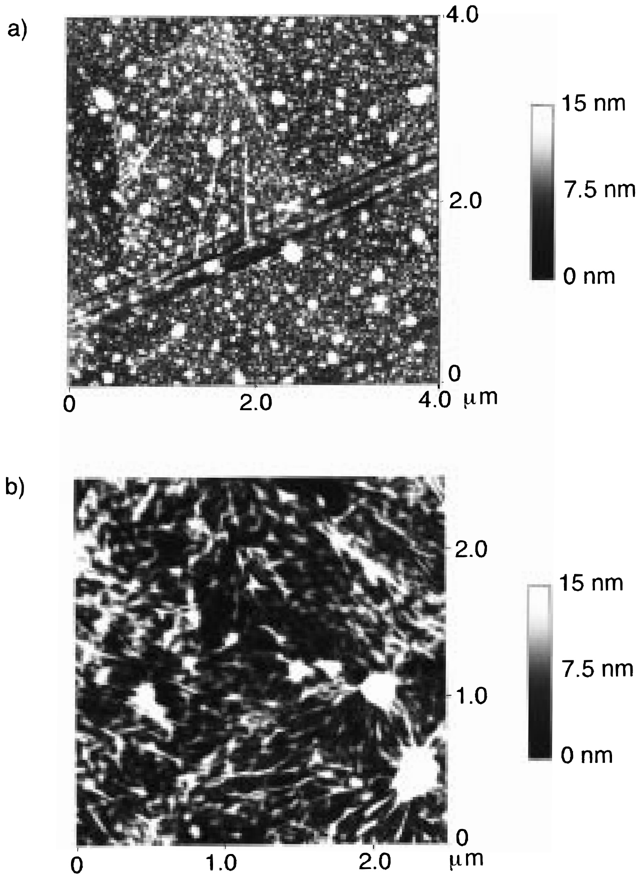

Figure 3. (a) Tapping-mode AFM image of the first graphite oxide layer deposited from the aqueous sol onto Al-coated glass and (b) image of a $(GO/PAH)_3GO$ film on Si(OH)/Al-Kg. *Z* range is 15 nm in both images.

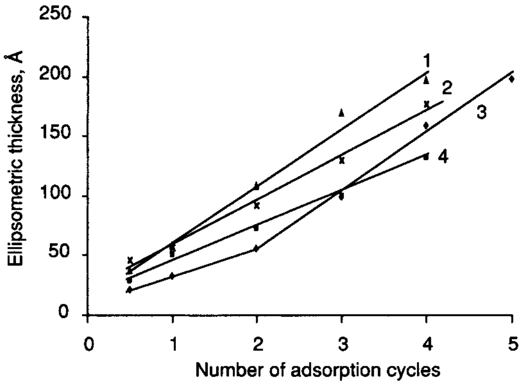

Figure 4. Ellipsometric measurements of the thickness of multilayer GO/PAH films vs number of adsorption cycles: 1, $Si(OH)/PAH(GO/PAH)_nGO$; 2, $Si(OH)/Al\text{-}Kg(GO/PAH)_nGO$; 3, $Si(NH_2)(GO/PAH)_nGO$; 4, $Si(NH_2)(GO/PAH)_nGO$ (pH 9). The thicknesses at an abscissa value of 0.5 correspond to primer cationic layers; points on the plots refer to films terminated by a GO layer.

plots indicates that on average the same amount of material is deposited in each adsorption cycle. However, for each the sample, the average increase in layer thickness per PAH/GO bilayer is different and ranges from 29 to 50 Å (Table 1). The lowest value, 29 Å per PAH/GO bilayer, is found for GO grown from aqueous ammonia solution (pH 9). The smaller layer pair thickness in this case may arise from partial deprotonation of the underlying PAH layer at this pH. Because the surface charge density is lower, fewer anionic sheets are bound by the polymer per unit area.

It should be noted that the measured thickness of the GO/PAH layer pair (40−50 Å) is more than that expected from the thickness of monolayer GO sheets (10.6−14.1 Å, as estimated by AFM for the first deposited GO layer, Figure 2a−c) and the thickness of single PAH layer (5 Å[24]). This can be explained in part by folding of the flexible GO sheets, which is apparent in the AFM images of all GO monolayers except the low coverage layer grown on $Si(NH_2)$. The multilayer adsorption model proposed by Kleinfeld and Ferguson for clay/polycation films[1b] may also be operative for GO/PAH. In their model, each adsorption cycle deposits about two layers of polyelectrolyte, but they rearrange (possibly by folding in the present case) into alternating single sheet/polycation films.

A plot of the thickness of a GO/PAH film grown from aqueous solution onto $Si(NH_2)$ is linear only after the third cycle. The average increase in thickness per PAH/GO bilayer is 23 Å in the first two adsorption cycles and 49 Å in the following three adsorption cycles (Figure 4). This behavior is reminiscent of that observed by Kleinfeld and Ferguson for clay/polycation films, which nucleate in islands and completely cover the surface only after several adsorption cycles.[25] We conclude that the GO/PAH film coverage is relatively complete after adsorption of the second bilayer (the first adsorption cycle covers ~30% of the surface; Figure 2a). In subsequent adsorption cycles, the layer pair thickness is close to that found for GO/PAH multilayers on Si(OH)/PAH. In the latter case, the surface coverage is ~85% after the first adsorption cycle, as shown in Figure 2c.

AFM. AFM images of four or five bilayer GO/PAH films on all three substrates were similar and did not clearly resolve the sheet edges or the voids between sheets. From these images, one can only conclude that the multilayer films completely cover the surface. Figure 3b shows a typical image of a $Si(OH)/Al\text{-}Kg/(GO/PAH)_3GO$ film. The average roughness of this film is 20 Å, which is consistent with a surface of loosely tiled and folded sheets. Multilayer film roughness and thickness parameters, determined by AFM and ellipsometry, respectively, are summarized in Table 1.

For all the substrates under investigation (except for very rough aluminum foil), GO/PAH multilayers deposited from aqueous sols on $Al(OH)_x$-terminated surfaces (Si(OH)/Al-Kg and Al/Al_2O_3) are smoother than those deposited on NH_2-terminated surfaces ($Si(NH_2)$ and Si(OH)/PAH) (Table 1). Comparing the surface morphologies of the first GO layer and the multilayer films, one can see that the more densely tiled first layer (~90%, Figure 2b), grown on the Keggin-primed surface, yields a smoother and more compact multilayer film, whereas the poorly tiled first layer (~35%, Figure 2a) on $Si(NH_2)$ yields the roughest multilayer surface. Again, this behavior is consistent with the model proposed by Kleinfeld and Ferguson for multilayer growth on islands, which eventually coalesce into smoother films.[25]

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[24] (a) Lvov, Yu.; Haas, H.; Decher, G.; Mohwald, H.; Kalachev, A. *J. Phys. Chem.* **1993**, *97*, 12835. (b) Lvov, Yu.; Decher, G.; Mohwald, H. *Langmuir* **1993**, *9*, 481, (c) Decher, G.; Hong, J.; Schmitt, J. *Thin Solid Films* **1992**, 210/211.

[25] Kleinfeld, E. R.; Ferguson, G. R. *Chem. Mater.* **1996**, *8*, 1575.

Table 1. Characterization of Multilayer GO/PAH Films by AFM and Ellipsometry

sample	average roughness of the anchored substrate surface, Å	average roughness of the film surface, Å	total film thickness, Å	average increase in film thickness per PAH/GO bilayer, Å
$Si(NH_2)/(GO/PAH)_3GO$	3.8	27	137	23 (first, second) 49 (third, fourth)
$Si(NH_2)/(GO/PAH)_3GO^a$	3.8	13	105	29
$Si(OH)/PAH/(GO/PAH)_3GO$	6.2	26	176	51
$Si(OH)/Al\text{-}Kg/(GO/PAH)_3GO$	4.3	20	130	38
$Glass/Al/Al_2O_3/(GO/PAH)_4GO$	35.0	22		
$Al\ foil/Al_2O_3/(GO/PAH)_4GO$	48.0	58		

[a] GO was adsorbed from aqueous ammonia solution (pH 9).

The most compact and smooth multilayer films are grown from aqueous ammonia solution (pH 9), from which very large (up to 9 μm wide) GO sheets are adsorbed. Each of these sheets covers an area which exceeds the area of voids between the sheets (see Figure 2d). Multilayer films grown on these large and smooth islands have the best overall quality.

In this connection, it is important to emphasize that the lateral dimensions of the GO sheets prepared by preoxidation and oxidation of natural graphite, followed by proper dispersion of the product GO, are significantly larger than those previously used for layer-by-layer assembly (50−150 nm)[7]. While there have now been many studies of exfoliated lamellar compounds,[4] it is rare that one find sheets with lateral dimensions exceeding 1−2 μm, even when the starting material consists of relatively large single crystals. The fragmentation of large individual sheets into submicron pieces may arise from mechanical stress during the exfoliation process. The factor that limits their lateral dimensions is probably the density of defects in the sheets, which apparently is quite low in GO prepared from natural graphite. The other important point to note is that complete oxidation is needed to make unilamellar GO as opposed to a suspension of graphite core/GO shell particles. This fact, and the higher dilution of the GO dispersions used in this study, may be the reason that the sheets in our monolayer films are thinner (10−14 Å) than those reported by Kotov et al. (18−27 Å).[7]

Multilayer films grown from unilamellar colloids of zirconium phosphate, layered transition metal oxides, and layered metal dichalcogenides typically have roughnesses on the order of the individual sheet thickness (0.8−1.6 nm).[5,6] In contrast, the relatively high roughness of the GO/PAH multilayers is most probably due to the flexibility of the GO sheets, which allows folding and turning up of the edges of the sheets. However, in the case of the relatively rough surface of the Al-coated glass, adsorption of the large GO lamellae and multilayer $(GO/PAH)_4GO$ films results in smoothing of the surface (Table 1).

Electronic Properties of GO/Polycation Films. The electrical characteristics of GO/polycation multilayer films were investigated with both electronically insulating (PAH) and conducting (PAN) polycations. For comparison purposes, a restacked GO colloid containing no polycations was also investigated. In all cases, the films were grown on ITO glass, and the top contact was Pt. ITO and Pt are respectively intermediate and high work function contacts, and both GO and PAN are good hole conductors. One would therefore expect that a rectifying contact could form between the film and ITO and that the forward bias direction would have the Pt electrode positve and ITO negative.

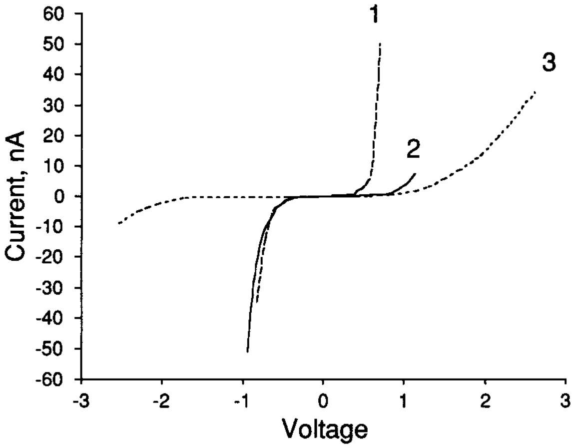

Figure 5. Current vs voltage characteristics of GO colloid and GO/polycation multilayer films deposited on ITO-coated glass: (1) 120-nm-thick $ITO-(GO/PAN)_{30}GO-Pt$ device; (2) 60-nm-thick $ITO-(GO/PAH)_{14}GO-Pt$; (3) 90-nm-thick $ITO-(GO)_x-Pt$. The positive direction on the voltage axis is ITO(+)/Pt(−).

All GO devices tested in this manner showed rectifying behavior (Figure 5). (An ITO/Pt control experiment gave the expected ohmic response). For the 60-nm-thick $ITO-(GO/PAH)_{14}GO-Pt$ device (curve 2), the "forward" (ITO(−)/Pt(+)) and "reverse" bias turn-on potentials were 0.42 and 0.82 V, respectively. These potentials correspond to electric fields, E, of 7.0×10^4 and 1.4×10^5 V cm^{-1}, respectively. When the conducting polymer PAN is substituted for PAH (curve 1), the forward bias turn-on potential is basically unaffected, but the reverse bias turn-on potential decreases to 0.41 V. In this case the electric fields required to obtain a current density of 5 mA cm^{-2} were 4.8 and 4.4×10^4 V cm^{-1} in the forward and reverse directions, respectively. These fields are 1−2 orders of magnitude smaller than those of single and bilayer polymer devices.[26] For both devices, the current follows the $\ln(I) \sim E^{-1}$ law, as expected for a tunneling-based charge injection mechanism. This is similar to the behavior observed for most single and bilayer polymer diode devices.

The resistivity of both the $ITO-(GO/PAH)_{14}GO-Pt$ and $ITO-(GO)_x-Pt$ devices is on the order of 10^6 Ω cm, and that of the thicker $ITO-(GO/PAN)_{30}GO-Pt$ device is approximately 1 order of magnitude lower. The

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(26) (a) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1998**, *365*, 628. (b) Vestweber, H.; Oberski, J.; Greiner, A.; Heitz, W.; Mahrt, R. F.; Baessler, H. *Adv. Mater. Opt. Electron.* **1993**, *2*, 197.

difference arises from the electronic conductivity of the PAN layers, which mediate electron transfer between GO layers. For both the GO/polycation and GO films, an irreversible conversion to a more conductive state occurs when the device is held at high current density. For ITO−(GO/PAH)$_{14}$GO−Pt and ITO−(GO/PAN)$_{30}$GO−Pt, this effect became noticeable at current densities of 17 and 70mA/cm^2, respectively. A similar effect begins at a current density of about 40 mA/cm^2 with ITO−(GO)$_x$−Pt. At current densities above 470 mA/cm^2, the current gradually increases by 3 orders of magnitude at constant voltage with the ITO−(GO/PAN)$_{30}$GO−Pt device. We tentatively ascribe this behavior to an internal electrochemical reaction, which reduces GO to a more conductive carbon-rich material. Apparently, the PAN samples are more resistant to this effect, possibly because the PAN itself acts as a reservoir of oxidizing equivalents. Similar electrochemical effects have been found with electrodes prepared from bulk GO[27] and were also observed by Kotov et al., in their study of GO/poly(diallyldimethylammonium chloride) thin films.[7]

Conclusions

We have shown that the quality and morphology of GO monolayer thin films depend on the source of graphite, its degree of oxidation, and the conditions used to prepare the GO colloid, as well as on the nature of the surface-priming layer and the pH of the adsorbing solutions. By properly controlling these parameters, one can select intact, unilamellar GO sheets and achieve reasonably dense (ca. 90%) coverage on a cationic surface. GO sheets prepared in this manner from natural graphite have larger lateral dimensions (1−9 μm) than any other lamellar inorganic colloid studied to date. The thickness of an individual GO layer, which can be fully exfoliated by means of preoxidation and oxidation steps, followed by appropriate dilution, is on the order of 10−14 Å

Multilayer GO/PAH films deposited in four or five adsorption cycles completely cover the surface of cationic substrates. The average roughness of these multilayer films is lowest when the GO suspension contains large sheets and when the coverage of the first layer of sheets is highest. However, sequential adsorption of GO and polycations invariably results in an average thickness change per adsorption cycle that is 2−3 times the monolayer thickness. This appears to occur because the flexible GO sheets fold and overlap on the surface.

The electronic characteristics of GO multilayer films contacted by ITO and Pt electrodes are consistent with its hole-conducting properties. By interleaving GO with poly(aniline), a hole-conducting polymer, the diodelike behavior of the films is retained, but the conductivity is increased by approximately 1 order of magnitude. Thin film GO devices are, however, irreversibly changed at high current density, most probably because of electrochemical reduction of GO to carbon.

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