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Elastic Properties of Dense Nanotube Layers

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Abstract—The Young modulus of a thin layer consisting of densely packed carbon nanotubes oriented normally to a substrate is measured using a scanning probe atomic force microscope. It is found that the adhesion of the film and the silicon substrate is not very strong, and, at certain conditions, this may lead to an intense energy dissipation in an oscillatory system loaded by the film. © *2001 MAIK "Nauka/Interperiodica".*

A great number of papers on the synthesis of carbon nanotubes and on the investigation of their physical properties were published after their discovery in 1991 [1, 2]. The interest to these objects is not incidental, since the prospects of their applications in technology are quite evident. Carbon nanotubes have unique electric, elastic, and mechanical properties; their cavities can be filled by atoms of various elements. For example, it was reported that an isolated nanotube can have a Young modulus along its axis greater than 1 TPa and a shear modulus of only 1 GPa simultaneously. The data reported by different authors strongly vary, which is most probably connected with the defects present in nanotubes. Now, it is possible to manufacture dense layers of nanotubes oriented normally to a substrate [3, 4]. Such layers proved to be effective cathodes for autoelectronic emission [5, 6]. At the same time, the investigation of the elastic and mechanical properties of dense layers of nanotubes is just at its starting point and is mainly of a theoretical character [7, 8]. In this paper, we report on the experimental studies of the elasticity of dense nanotube layers and the dissipation of the energy of elastic vibrations in them. First, we describe the results of measurements performed with the help of a scanning probe atomic force microscope and, then, the results of measurements of the Q factor of a macroscopic oscillating system loaded on a sample with a carbon nanotube film.

A nanotube layer with the thickness 142 nm was obtained by the deposition of carbon atoms on a silicon surface in the process of electron-beam evaporation of pure graphite in vacuum. The layer was a mixture of multilayer nanotubes with the diameters from 3 to 5 nm and single-layer tubes with the diameter of 1.1 nm. The tubes formed a fiber texture with the axis normal to the substrate surface.

A NanoScan measuring device was used in the studies by scanning probe microscopy. The device is described in detail in a review [9]. An oscillating system (a tuning fork) operating at a frequency of 20 kHz was loaded through a vibrating diamond stylus on various materials. The stylus pressing upon the substrate could be smoothly adjusted with the help of a piezoelectric control system. The displacement of the tuning fork reed, to which the stylus was fixed, was monitored with the precision up to 0.1 nm. The device could operate in two modes. In the first case, the shift of the resonance frequency in a self-oscillating system was measured. Here, the major contribution to the response (the frequency change) was provided by the elastic properties of the sample under test. Further, we will refer to this case as to the mode of "elasticity measurements." In the second case, the decrease that occurs in the vibration amplitude due to the contact with the substrate is measured. The dissipative processes are very important in this case, and, hence, it will be conditionally referred to as the mode of "viscosity measurements."

A stylus with a large enough curving radius was selected to measure the macroscopic characteristics of the sample by averaging over the area of tens of nanometers (this is important while working with nanotubes). The study of the surface relief showed that the surface of the nanotube film was smooth. There were single steps, protrusions, and indents with the height of several nanometers (Fig. 1). Small areas with special properties can sometimes be observed, which can be identified as the specks of the graphite phase.

The main results of the measurements are as follows. The dependences of the parameters of the oscillating system on the deformation (deepening of the stylus into the sample) were recorded. Generally speaking, the dependences of this type, which describe the response of various parameters of the system to the change of conditions at contact are usually called the loading curves. (The most standard case of a loading curve is the dependence of the sample deformation on the load.) A diamond stylus was pressed into the sample under a smoothly varying external load and deformed it. In the mode of elasticity measurements, a smooth change of the resonance frequency f relative to the resonance frequency f_0 in air is observed in the process of stylus pressing. We proceed from the standard Hertz approximation [10]. We assume that the stylus point can be treated as a hemisphere with the radius R. We also assume that its Young modulus is greater than the corresponding moduli of the materials under test. In the case of a nanotube layer, this assumption is substantiated by [8]. Moreover, the validity of this assumption is substantiated by the results of measurements. Under these conditions, the frequency shift is equal to

$$f - f_0 = \frac{f_0}{k_0}\sqrt{R}\frac{E}{(1-\nu^2)}\sqrt{h}. \quad (1)$$

Here, k_0 is the elasticity coefficient of the oscillating system, E is the Young modulus of the tested sample, ν is the Poisson ratio of the sample, and h is the displacement of the tuning fork reed in the process of the stylus pressing.

Figure 2 presents the dependence of the quantity $(f - f_0)^2$ on the displacement of the tuning fork reed for three different samples. In the plot under consideration, this dependence for a homogeneous sample must be linear. In fact a dependence close to a linear one is observed for a (100)-cut silicon plate and glass. One has to keep in mind that the stylus point can be treated as a hemisphere only with a certain reservation. The relationship between the elastic constants, which is obtained from Eq. (1) and Fig. 2 for silicon and glass, agrees well with reference data. This allows one to conduct measurements on samples with unknown elastic moduli and determine their elastic parameters using Eq. (1) from the comparison with reference samples.

The properties of a nanotube layer deposited on silicon are of a major interest for us. In this case, a difficult problem that is not yet solved arises, namely, the problem of the relative contributions to the loading curve from the film and the substrate in the case of a layered system. We proceed from the fact that the penetration depth H of the deformation into a sample is about the radius of the contact area between the stylus and the sample in order of magnitude. Then, according to the Hertz theory, we have

$$H \approx \sqrt{Rh}. \quad (2)$$

When $H \leq d$, where d is the film thickness, the behavior of the system is determined by the properties of the nanotube layer. When $H \gg d$, the system properties are governed by the substrate elasticity.

We observe this behavior in Fig. 2. The inclination angle of the loading curve for the layered structure is constant at small loads, and it is greater than the angle for glass but smaller than in the case of silicon. Only the elastic properties of the film are important in this region. In the case of large values of h, the inclination of the loading curve becomes the same as for silicon, and the elastic reaction of silicon becomes decisive.

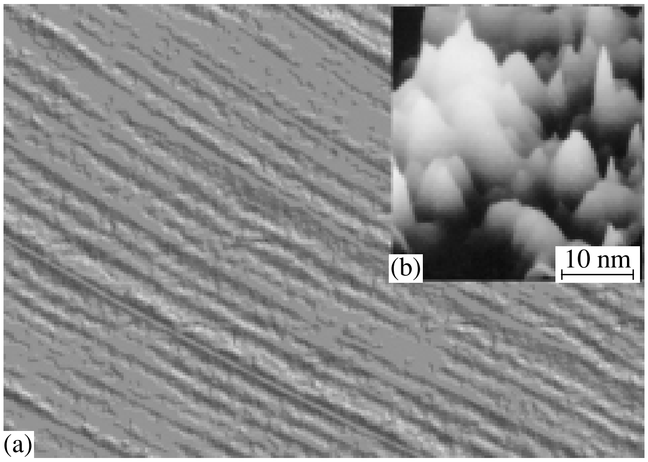

Fig. 1. (a) Surface relief of a carbon nanotube film observed by a scanning atomic force microscope. The area is 5 × 7 μm^2, and the height difference is about 10 nm. (b) Surface relief of a carbon nanotube film observed by a scanning tunneling microscope with a resolution of 1 nm, which provides the observation of individual nanotubes.

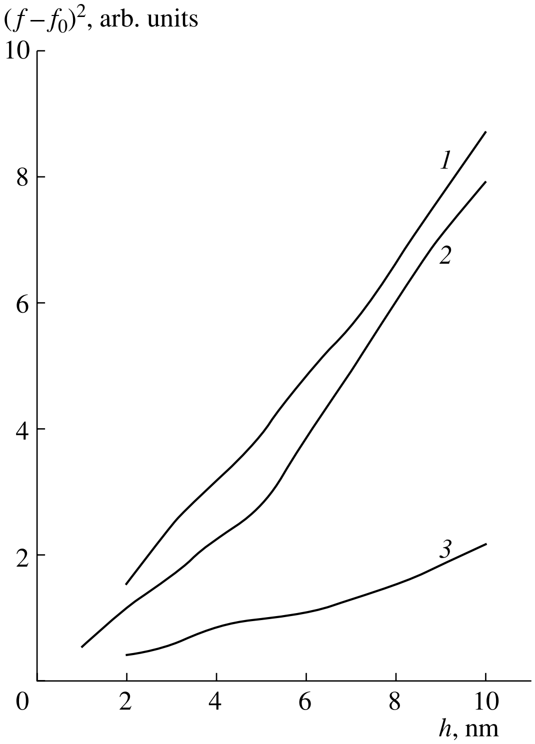

Fig. 2. Square of the frequency shift in an atomic force microscope versus the pressing depth for (*1*) silicon, (*2*) silicon with a nanotube layer, and (*3*) glass.

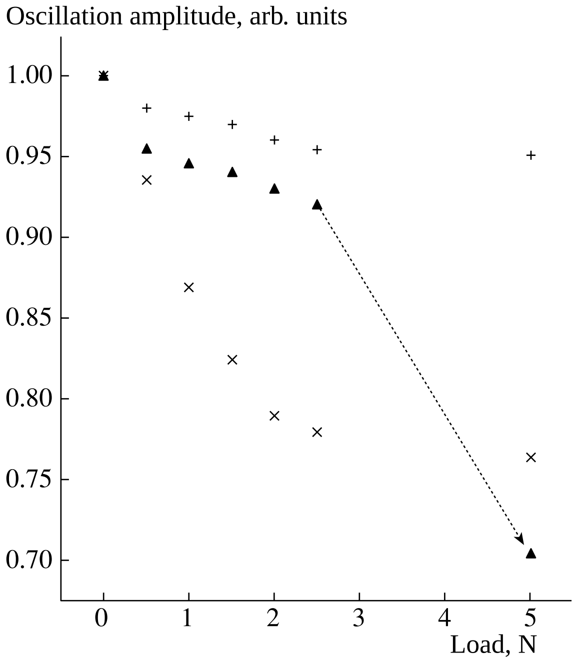

Fig. 3. Oscillation amplitude of a macroscopic oscillatory circuit versus the load: (+) silicon, (▲) silicon with a nanotube layer, and (×) plexiglas.

Using $h = 4$ nm as an approximate limiting point of the region where the role of the substrate is not yet significant, we can estimate the order of magnitude of the effective curving radius of our stylus from the condition $H \approx d$: $R \approx 5$ μm, which agrees qualitatively with our data on the stylus.

The comparison of the loading curve for silicon and the loading curve for the nanotube layer at small loads (when the role of the substrate is small) gives $E/(1 - \nu^2) \approx 140$ GPa for the nanotubes. According to the theoretical calculations [8], the Poisson ratio for a layer of nanotubes oriented normally to the surface, when the pressure is also normal to the surface, is small enough ($\nu \ll 1$). This means that it is possible to estimate $E \approx 140$ GPa. It is interesting to compare at least qualitatively this result with the theory. The Young modulus was calculated in [8], but it was obtained for a “crystal” of ideal single-layer nanotubes arranged in a triangular grid and oriented strictly parallel to each other. It turned out that, in the case of an experimental geometry analogous that used by us, the Young modulus along the axes of single-layer tubes 3 nm in diameter is close to 300 GPa, and, when the tube diameter is equal to 5 nm, the corresponding Young modulus is approximately 200 GPa. At the same time, the Young modulus across the tubes is as small as several gigapascals. Such a disagreement with our experiment is natural. Although the investigated film belongs to the best samples manufactured up to now, it consists of a mixture of multilayer tubes of different diameters with an admixture of single-layer tubes. Therefore, the tubes do not form an ideal triangular grid. Moreover, the stylus in the atomic force microscope is inclined to a certain extent with respect to the substrate plane, which introduces some distortions due to the strong asymmetry of the Young modulus.

It is necessary to note the excellent mechanical properties of the nanotube layer. Visible fracture of the film was observed only in the case of pressing of the stylus approximately to a depth of 100 nm, which was comparable with the film thickness.

Measurements of the oscillation amplitude as a function of the penetration of the stylus into the sample were also conducted. It is difficult here to obtain unambiguous information on the film properties. Several dissipation mechanisms come into play simultaneously (the adhesive friction, the water layer at the boundary, the viscoelasticity, etc.). In certain conditions, the processes caused not by the dissipation but by the equipment-related factors can also be partially responsible for the amplitude decrease in the atomic force microscope [11]. Here, we only note the following important fact. The amplitude decrease that occurred at the contact with the nanotube film turned out to be comparable to the decrease observed in the case of pure silicon. This means that we did not observe any unusually strong loss mechanisms by the atomic force microscopy.

We measured dissipative losses in a series of materials by a device that was a macroscopic analog of the probe of our microscope and that was developed much earlier under the name of a contact impedance meter [12]. An oscillatory circuit with the Q factor at least one order of magnitude higher than that of the atomic force microscope was loaded on a test sample through a steel ball. It was possible to detect the changes in both frequency and amplitude and to determine the elastic and dissipative parameters of the material. The region of deformation was greater than the film thickness because of the large diameter of the ball that was in contact with the sample (about 0.5 mm), and our oscillatory system was not suitable for the determination of the elastic constants of the layer. Therefore, the study was conducted only in the viscosity measurement mode (the measurement of the oscillation amplitude with the ball being pressed into the sample). The results are presented in Fig. 3. The load is plotted along the abscissa axis, and the oscillation amplitude reduced to the amplitude of the unloaded oscillatory system is plotted along the ordinate axis.

We stress that our device measured the dissipation in the sample rather than its elastic properties, and this fact was specially verified in our experiments. Figure 3 gives the data for silicon. However, they coincide within the precision of measurements with the data for the materials that are quite different in their elastic properties, such as glass, aluminum, and brass. It would be impossible to distinguish them in our plot. We took also viscoelastic materials for comparison. The data for plexiglas are given in Fig. 3 as an example.

Now let us consider the basic result, i.e., the measurements performed for a nanotube layer on silicon. In the case of a weak pressing, the dissipative losses are not large, though they are distinctly larger than for pure silicon. However, when the load increases, a sharp growth of losses was observed (a sharp decrease in amplitude is indicated by the line connecting neighboring points in the drop region). Regretfully, it was impossible to use loads greater than 2.5 N without taking the risk to smash the sample. It was possible only to use a load of 5 N with the application of a special gadget. That is why only a small number of points was obtained in the most interesting region.

Such a sharp growth of losses can be connected with the temporary local separation of the nanotube layer from the silicon substrate because of the insufficiently strong adhesion. The most probable reason for such separation is the presence of the tangential component in the forces caused by the ball pressure on the sample. Elastic vibrations of the system lead to a relative motion of the film and the substrate in the separation region and to energy losses due to the friction. Since the contact region is large in our case, the energy losses can be considerable. Moreover, the film separation from the substrate also leads to the displacement of nanotubes with respect to each other (the lower part of a tube is no more fixed to the substrate, and the bond between the tubes is fairly weak). We also cannot exclude the influence of this factor on the absorption of the elastic vibrations.

Qualitative estimates show that a sharp growth of losses occurs in our experiment when the tangential stresses at the film–substrate interface reach several tens of megapascals. In view of the high normal pressure applied at the symmetry axis of the system (up to several gigapascals), this result indicates a not very strong adhesion of the film and the substrate. Nevertheless, it is necessary to take into account that the separation can occur away from the symmetry axis, i.e., outside the region of the strongest pressing.

Performing repeated measurements, we obtained the same results as in the first measurement (for all values of the pressing force). If the film were unable to restore its initial bonds with the substrate, the subsequent measurements would differ from the initial ones. A good review of a very complex and interesting problem of adhesive friction, which may help to understand the problem, can be found in [13].

Measurements with a separated nanotube film of an analogous composition were also conducted. As expected, we observed a strong absorption, which far exceeded the absorption given in Fig. 3 already at small loads. This fact demonstrates once more that, if the separation were retained after the first measurement, the absorption in the repeated measurements would be greater.

It is important to note that, in some regions on the surface, no noticeable damping of vibrations could be observed at any applied loads. This is the evidence of a strong adhesion of the film and the substrate in these regions. Therefore, it is possible to obtain a strong adhesion of a nanotube film and a substrate with improved technology. The technique used in this study can be a good method of monitoring the film adhesion.

As a result of the investigation of a thin film of densely packed carbon nanotubes, it became possible to measure the Young modulus of the film, which is an important parameter from the point of view of future applications and which widely differs from the Young modulus of individual nanotubes and nanotube ropes [14, 15]. It was demonstrated that the adhesive bond between a film and a silicon substrate was not very strong for the major part of our sample. However, in some regions, this bond is strong enough, which means that it is possible to create layered structures with high mechanical stability by introducing the necessary improvements in the growth technology.

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