CONF-961202--90 SAND97-0479C

GROWTH AND MECHANICAL AND TRIBOLOGICAL CHARACTERIZATION OF MULTI-LAYER HARD CARBON FILMS

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ABSTRACT

Vacuum-arc deposition is used to deposit multilayer carbon films by modulating the sample bias during deposition. The effect of varying the sublayer thickness in multilayer films consisting of alternating layers of "hard" (68.4 GPa, -100 V bias) and "soft" (27.5 GPa, -2000 V bias) was investigated. Films consisting of equal thickness layers of hard and soft material and an individual layer thickness varying from 10 to 35 nm were deposited. Mechanical property measurements were obtained by finite element modeling of nanoindentation load-displacement curves. The film hardness values were about 20% below the average of the component layers and relatively independent of the layer thickness. TEM investigation revealed deterioration of the multilayer structure when the sublayer thickness was below 15 nm due to implantation damage of the hard layers caused by the energetic C^+ ions of the soft layers (-2000 V bias) deposited over them. Pin-on-disk wear tests show that the wear rate drops when sublayer thickness is decreased below 20 nm and remains constant with further decreases in the layer thickness.

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INTRODUCTION

Amorphous carbon films with a maximum hardness of nearly 70 GPa can be grown by vacuum-arc deposition [1]. The practical use of these films is limited by the large residual compressive stresses (>10 GPa) in the hardest films which can lead to delamination [2]. Stress is linearly correlated with hardness in these films [3,4] and appears to be an intrinsic attribute of the ion-beam growth process that leads to hard films [1,4]. Previous work in our laboratory has shown that multilayer carbon films consisting of alternating layers of hard (~60 GPa) and softer (~30 GPa) material can have lower compressive residual stresses while retaining hardnesses above 30 GPa [5]. The wear rates of the multilayer films were found to be unusually low ($<10^{-7}$ mm^3 N^{-1} m^{-1}) and, at high loads, tribological performance was shown to be optimized for multilayer films with an approximate 50:50 hard:soft thickness ratio [6]. We investigate here the effect of the thickness of the individual layers on the hardness and wear rates of multilayer films of this structure.

EXPERIMENTAL

The deposition method has been described in detail elsewhere [5,7]; only a summary will be presented here. C^+ ions are extracted from a vacuum-arc plasma and passed through a

Proceedings of the Fall MRS, Symposium A, in press

magnetic particle filter. The incident energy of the C^+ ions is ca. 20 eV. Additional ion energy is added by negatively pulse biasing the substrate with a 25% duty cycle. The mechanical properties of films made at -100 V and -2000 V sample bias are given below. The soft layer is deposited first, and alternating hard and soft layers are deposited sequentially. The final deposition is a hard layer. All films studied here were deposited on Si (100) substrates. The relative densities of the two layers are considered when designing films with equal thicknesses of hard and soft material.

Table 1. Mechanical properties of monolithic vacuum arc carbon films. The density and stress measurements are from [7] and [8], respectively. The nanoindentation measurement is from this work and is described below.

Deposition conditions	Yield stress (GPa)	Young's modulus (GPa)	Hardness (GPa)	Compressive film stress (GPa)	Density (g/cm^3)
-100 V, 25 % duty cycle	49.1±2.9	848±10	68.4±2.5	10.5	3.0
-2000 V, 25% duty cycle	14.1±0.4	360±10	27.5±0.7	3.0	2.1

The hardness of the films is obtained using finite element modeling of load-displacement curves obtained with a commercial nanoindenter [9]. The methodology has been used to extract reliable hardness values for thin films at indentation depths up to 50% of the layer thickness [10]. Wear data was obtained by a pin-on-disk tester with a 6 mm diameter ruby pin. The films were tested in air with 30% relative humidity at a 240 g load (2.4 N).

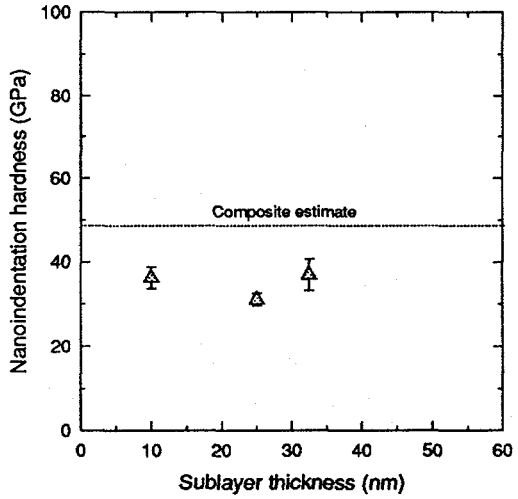

Fig. 1. The effect of sublayer thickness on the nanoindentation hardness of multilayer carbon films. The film with 32 nm sublayer thickness consists of 8 sublayers (4 hard, 4 soft). The other two films are 10 sublayers thick. The hardness value for the 8-layer film is from [5].

RESULTS AND DISCUSSION

The hardness as a function of sublayer thickness for three 50:50 hard soft films is shown in Fig. 1. In all cases the hardness of the multilayer film is less than the average of the monolithic hard and soft values, 48 GPa. Figure 2 compares the multilayer structure of two films with a sublayer thicknesses of 30 nm and 15 nm, respectively. In the case of 30 nm

films with a sublayer thicknesses of 30 nm and 15 nm, respectively. In the case of 30 nm layers, the multilayer structure is clearly visible. This film was deposited with approximately equal mass densities of hard and soft material [5], rather than with equal thicknesses as in this work. Therefore, the layer thickness ratio is 40:60 hard:soft. The multilayer structure of the 15 nm film is not visible. The dark band above the substrate is assigned to a hard layer; the light area above is attributed to hard material that has been damaged by ion implantation from the -2000 eV C^+ ions of the soft layer. T-DYN 4.0 simulations [11] of the deposition and implantation process predict that the 2 keV ions from soft layer deposition can penetrate 5-10 nm into the hard layer. The individual hard layer in the film in Fig. 2(b) should be ca. 15 nm thick, on the order of the 2 keV C^+ ion penetration depth. We attribute the loss of a well-defined multilayer structure to implantation damage. We find that in the case of very thin sublayers (i.e., <15 nm) it will not be possible to make carbon multilayer structures with well-defined interfaces using 2 keV C^+ ions for the soft layer. Interestingly, the loss of multilayer structure does not have a large effect on the hardness. Figure 1 shows that the hardness values for the films with 10 nm sublayers (no multilayer structure expected) and with 31 nm sublayers [multilayer structure shown in Fig 2(b)] are within 10% of each other, which is within the overall uncertainty of the measurement.

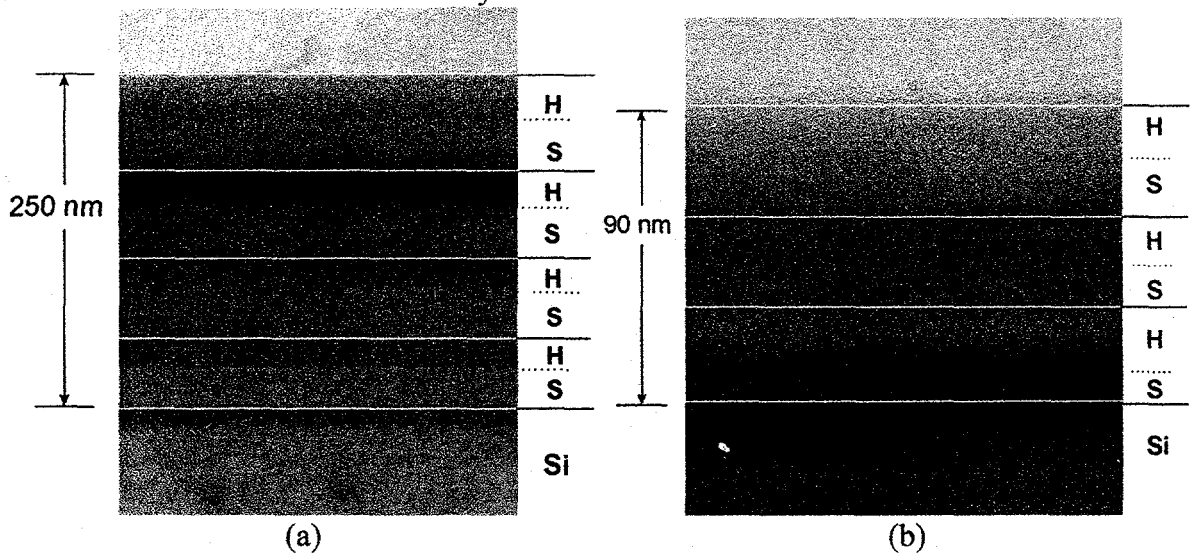

Fig. 2. TEM images of multilayer carbon films, "hard" layers are distinguished by their higher density (darker): (a) nominal sublayer thickness = 31 nm, the multilayer structure is clearly visible, actual film thickness ratio is 40:60 hard:soft [5]; (b) sublayer thickness = 15 nm, multilayer structure not visible.

The relative wear rates of a series of 100 nm thick films with varying sublayer thickness were measured. Because the films were thin, it was difficult to observe a wear track before the film wore through to the substrate. Therefore, the wear resistance of this set of multilayer films was evaluated by measuring the number of cycles required to wear completely through the film. The wear-through point was defined by the large increase in friction coefficient (from <0.1 to ca. 0.5) caused by contact of the ruby pin with the Si substrate. The number of cycles to wear through the film, normalized to the film thickness as determined by Rutherford Backscattering, is shown in Fig. 3. The wear rate of the multilayer films with thinner sublayers is lower than that of the monolithic hard film. The wear resistance is improved when the sublayer thickness is 20 nm or less. It has been

similar to the trend observed here, but it is not clear that the wear rate here is controlled by the yield stress of the films. In fact the yield stress measured by the nanoindentation modeling, 49.1±2.9 GPa, for the monolithic hard film is much larger than the values observed for multilayer films, 15 - 18 GPa, which have lower wear rates.

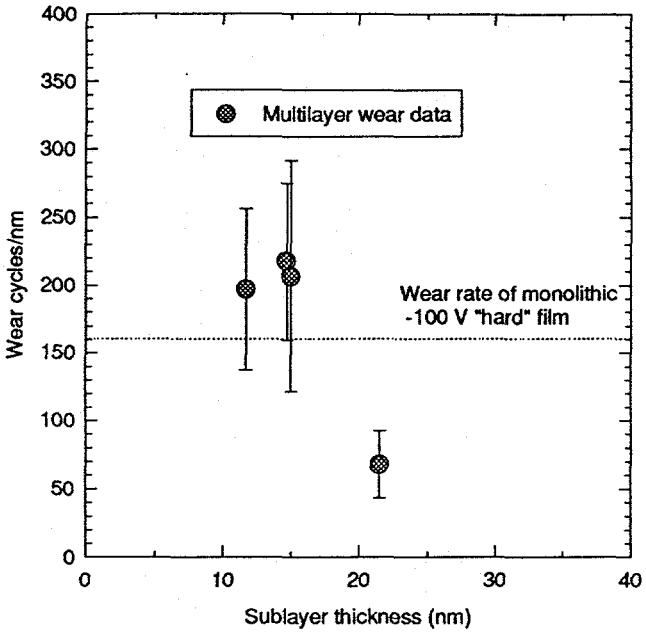

Fig. 3. Wear rate of ca. 100 nm thick multilayer carbon films as a function of sublayer thickness. The dotted line is the wear rate of a ca. 50 nm thick monolithic "hard" film.

CONCLUSIONS

Multilayer hard carbon films were made with alternating layers of hard (68.4 GPa) and soft (27.5 GPa) material. The effect of sublayer thickness on the mechanical properties of multilayer films of equal thicknesses of hard and soft material was investigated. Film hardness was found to be relatively independent of sublayer thickness. In films with a sublayer thickness below 15 nm, the sublayers were not well-defined. This effect was expected and is attributed to ion implantation damage. Decreasing the sublayer thickness was observed to have a beneficial effect on wear. Films with sublayer thicknesses below 20 nm had wear rates substantially lower than both monolithic hard films and multilayer films with thicker sublayers.

ACKNOWLEDGMENTS

This work is part of "Processing for Surface Hardness" in the DOE Center for Excellence in Synthesis and Processing of Advanced Materials and was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, of the U.S. Department of Energy, under contract No. DE-AC03-76SF00098. All ion beam analysis was performed at the Los Alamos Ion Beam Materials Laboratory. This work was also supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

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