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Microhardness Studies on Thin Carbon Films Grown on P-Type, (100) Silicon

Joseph C. Kolecki
Lewis Research Center
Cleveland, Ohio

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MICROHARDNESS STUDIES ON THIN CARBON FILMS GROWN ON P-TYPE, (100) SILICON

Joseph C. Kolecki
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

A program to grow thin carbon films and investigate their physical and electrical properties has been started at NASA Lewis Research Center. This paper presents characteristics of films grown by rf sputtering and vacuum arc deposition on p-type, (100) silicon wafers. Microhardness data were obtained from both the films and the silicon via the Vickers diamond indentation technique. These data show that the films are always harder than the silicon, even when the films are thin (of the order of 1000 Å). Vacuum arc films were found to contain black carbon inclusions of the order of a few microns in size, and clusters of inclusions of the order of tens of microns. Transmission electron diffraction showed that the films being studied were amorphous in structure.

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INTRODUCTION

The growth of crystalline carbon films in vacuum has long been regarded as a theoretical possibility, though success in achieving it has been limited. Such films, referred to as diamondlike, would have practical applications as abrasion resistant coatings and, when doped with elements like boron, as semiconductors, where the high thermal conductivity associated with the diamondlike nature of the film would allow ready power dissipation. A program to grow carbon films and investigate their physical and electrical properties has been started at NASA Lewis Research Center. This paper is concerned chiefly with Vickers microhardness studies of carbon films grown on crystalline silicon substrates. Gambino and Thompson, in a paper on spin resonance spectroscopy (ref. 1), include a curve of Vickers microhardness versus load, which differs somewhat in numeric values but shows trends very similar to those being reported here. In general, it appears that the microhardness of the carbon films exceeds that of the silicon over a film thickness range of 1200 to 4600 Å. The films reported by Gambino and Thompson, and those reported in this paper, were all amorphous.

EXPERIMENTAL

Microhardness was measured by the Vickers diamond indentation method. This method consists of loading a small diamond-tipped stylus with a known weight and allowing it to penetrate freely the surface of the material being measured (fig. 1, ref. 2). The indentation, when viewed from above, is a square with well defined diagonals.

Measurement of the diagonal length and use of a conversion table yields a numerical value of microhardness with units of kilogram per square millimeter (kg/mm^2). Because the indent size is of the order of micrometers, a microscope with a reticle eyepiece is used to perform this measurement. The actual measurement of carbon film and silicon substrate microhardness was

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performed with a Buehler Micronmet Microhardness Tester (ref. 3). Stylus loads in these measurements ranged from 25 to 200 g.

Carbon films were grown by two techniques: RF sputter deposition with a carbon target and 45- to 50-μm backpressure of methane gas and vacuum arc deposition using a carbon arc operating in a background pressure of 10^{-5} to 10^{-6} torr at approximately 22 V and 50 A (ref. 4). The silicon substrate material was polished p-type silicon, with an electrical resistivity of 2- to 7-Ω cm and with a (100) surface orientation. Silicon was chosen because of the readiness with which the carbon films grew and adhered (ref. 4). Glass and metal substrates were also tried, but with limited success. Films grown on glass and metal fractured and spalled much more frequently than those grown on silicon, and their adhesion was usually poor. Hardness measurements were performed on both the carbon films and on the silicon substrates. Additionally, film step heights and surface profiles were obtained with a Tencor Alpha-Step Surface Profiler (ref. 5).

RESULTS

Vickers microhardness measurements were performed on the (100) silicon substrates and on the deposited carbon films, making careful note of the orientation of the indent with respect to the (100) surface axes of the silicon in all cases (fig. 2). When the diagonals of the indent were parallel to the surface axes, the orientation was taken to be 0°; otherwise, the orientation was taken to be the smallest angle formed by the diagonals and the surface axes. This definition works well for the case of a (100) surface since the axes in this surface are orthogonal. When other surfaces are used (such as (111) in which the axes are trigonal), some other definition must be provided, or more practically, a different indenter, such as a Knoop indenter (ref. 2), substituted for the Vickers indenter.

The measured microhardness of the silicon for a given load was found to vary with orientation, increasing in value with the angle (fig. 3). Corner cracking and concoidal edge fracturing also became more severe with increasing angle. It was found that at 0°, a clean indent with some corner cracking and essentially no edge fracturing was obtained. In this orientation, a 200-g load yielded a microhardness of ∿930 kg/mm^2. When the indenter was rotated to ∿20°, the amount of corner cracking and edge fracturing increased, and the 200 g load yielded a microhardness of ∿980 kg/mm^2. When the indenter was further rotated to 45°, the combined effects of cracking and fracturing became so severe that often no measurement could be made. Where measurement was made, 200 g yielded a microhardness ∿1050 kg/mm^2. Damage to the silicon substrate occurred in this orientation even when the indent was made in an overlying carbon film rather than directly on the silicon surface.

Two sets of microhardness data are presented in figure 4. Figure 4(a) shows data for an rf sputter-deposited film 3500 Å thick, taken with the indenter oriented at 0°; figure 4(b) shows data for an rf sputter-deposited film 4100 Å thick, taken with the indenter oriented at ∿30°. Data for the p-type (100) silicon substrates at the same respective indenter orientations are also given.

In the data of figure 4(a), the numerical value of microhardness is seen to increase with decreasing load below a load of 100 g for both the film and the substrate. This effect is discussed for brittle crystalline substrates by Brookes (ref. 6). Applying Brookes' argument, surface lattice damage, resulting from the (100) silicon surface being polished to a mirror-like

finish before deposition, can be assumed to result in the surface being somewhat harder than the underlying bulk material. Larger loads cause the indenter to penetrate more deeply into the bulk material so that more of the bulk characteristics are seen. Smaller loads, on the other hand, penetrate less deeply so that as the load is decreased, more and more of the surface characterisitics come into view. The bars in this figure represent standard deviations calculated from 18 to 24 measurements per datum.

In the data of figure 4(b), the numerical value of microhardness is seen to increase with decreasing load for the carbon film, but not for the silicon substrate. The behavior of the carbon film is not significantly different in this case than in the case of figure 4(a). Since the change of indenter orientation affects the silicon only, it may be inferred that the film behavior shown is indeed characteristic of the carbon film itself. The behavior of the silicon is also interesting because, if surface lattice damage is indeed a factor in the measurements, its effects are not so readily apparent here as in figure 4(a). Since the indenter orientation has this effect, it might be that surface cleavage is also playing a part in these measurements.

The shape of the film curves in figure 4 is explained by considering the depth-of-stylus-penetration to film-thickness ratio for a given stylus load. If this ratio is much greater than unity, the stylus has penetrated well into the substrate and the resultant measurement might be expected to be more characteristic of the substrate than of the film. If the ratio is small, on the other hand, the stylus has seen less of the substrate and, consequently, the measurement may be expected to be more characteristic of the film itself. For the geometry of the diamond indenter used here (ref. 2), the ratio of stylus penetration to film thickness can be shown to vary from $\sim$10:1 for a 1200 Å film with a 200 g load to $\sim$1.2:1 for a 4600 Å film with a 25 g load. Thus, the hardness numbers obtained from thick films under light load are probably most characteristic of the carbon films alone. Nonetheless, even thin films under heavy load showed small differences in hardness from the underlying silicon always in the direction of greater film hardness.

Film samples were subjected to electron diffraction and electron microscopy. Preparation for electron diffraction involved dissolving the silicon substrate so that the carbon film would float freely. Transmission electron diffraction patterns could then be obtained. A typical pattern is shown in figure 5. The obvious lack of well-defined spots and/or sharp rings indicates an amorphous structure. The actual surface structure is seen in the scanning electron micrograph (taken at 10,000X) of figure 6.

More data of microhardness versus load for rf-sputtered carbon films, ranging in thickness from 1200 to 4600 Å, are presented in figure 7(a). These data were all taken with the indenter oriented at 0°, and all show the same variation with decreasing load seen previously. Data for silicon at 0° are included for comparison. A crossplot showing microhardness versus film thickness (fig. 7(b)) shows no appreciable variation except for a slight increase of microhardness with increasing film thickness.

Carbon films grown on silicon with the vacuum arc were also measured. (The arc configuration used is fully described in ref. 4). These films had many dark inclusions which appeared to be bits of black carbon or graphite and which probably resulted from particulate ejecta from the cathode. Inclusions ranged in size from a few tenths to several micrometers. Clusters of inclusions also occurred, some being a loose aggregation of smaller individuals, others being large, tight, opaque islands. Clusters ranged in

size from 10 to 50 μm. The rf sputter grown films, by comparison, contained no such inclusions or clusters. A trace of a vacuum arc film profile (fig. 8) shows that individual inclusions often protruded several tenths of a micrometer above the surface of the film.

Attempts to measure microhardness of clusters were not successful since the clusters were torn away by the indenter stylus, leaving a hole in the film. Data were successfully collected from the clear regions between inclusions and clusters, and typical data are presented in figure 9. These data were obtained from a film 2800 Å thick. No essential differences in behavior from the RF sputter grown films of the previous figures are evident. As before, the indenter orientation was 0°. The corresponding curve for silicon is included for comparison.

CONCLUSIONS

Microhardness data were obtained from thin carbon films grown on p-type, (100) silicon of 2- to 7-Ω-cm electrical resistivity using rf sputter and vacuum-arc deposition. These data show that the film hardness is somewhat greater than that of the (100) silicon for a film thickness range of 1200 to 4600 Å and a load range of 25 to 200 g. Film hardness numbers were found to increase with decreasing indenter load for all orientations of the stylus with respect to the (100) surface axes of the silicon, and showed a weak tendency to increase with film thickness over these same ranges. Radio-frequency sputter-deposited films were found to be considerably more uniform in structure than vacuum arc-deposited films in terms of black carbon and/or graphite inclusions, which occur in large quantities in the vacuum arc films. Both the rf and the vacuum arc films were found to be of comparable hardness, however. Transmission electron diffraction patterns, obtained after the silicon substrates were dissolved away, showed that the carbon films were amorphous in structure.

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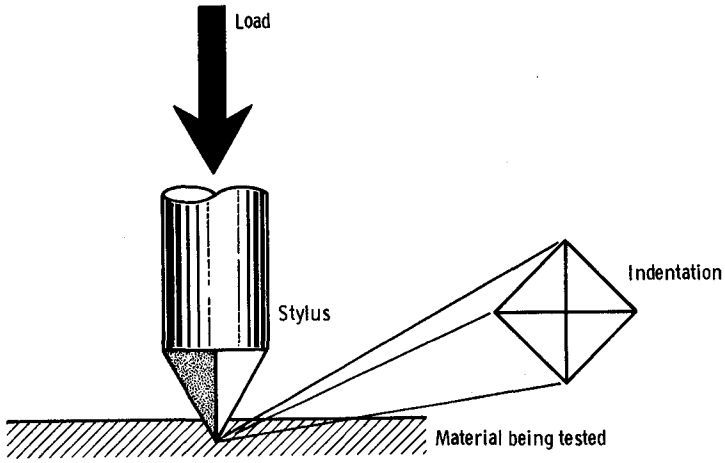


Figure 1. - Indentation hardness testing.

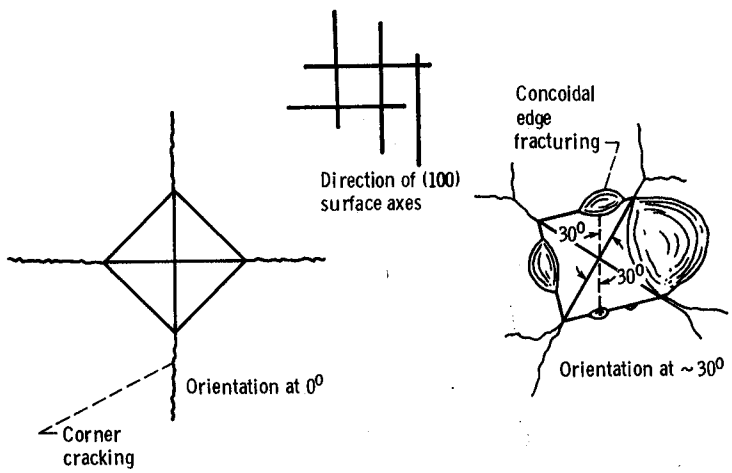


Figure 2. -Indenter orientation effects.

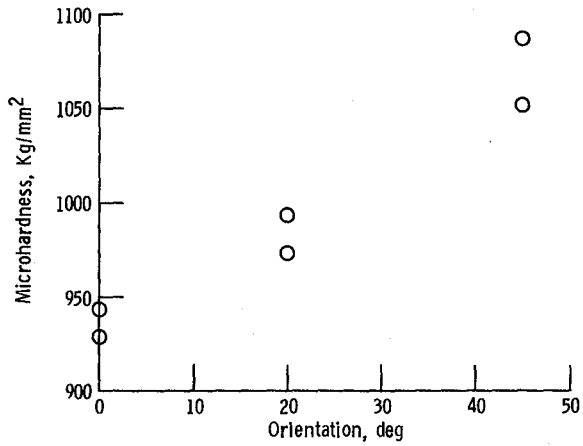


Figure 3. - Variation of microhardness with indenter orientation measured with a 200 gm load.

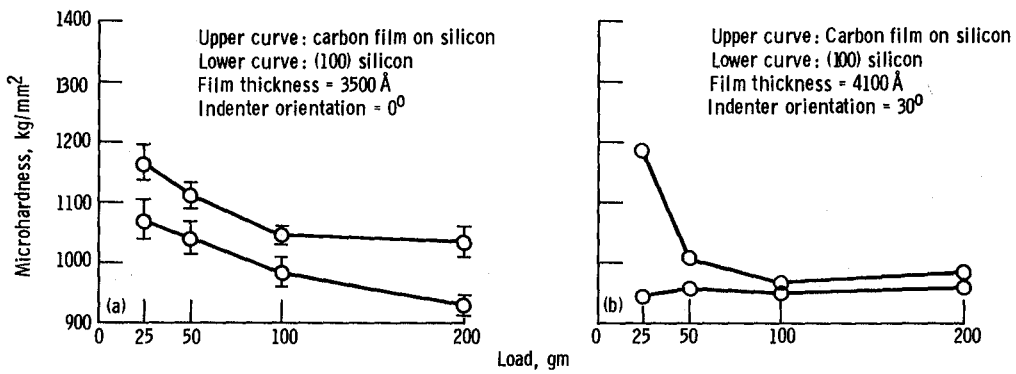


Figure 4. - Plots of microhardness vs load.

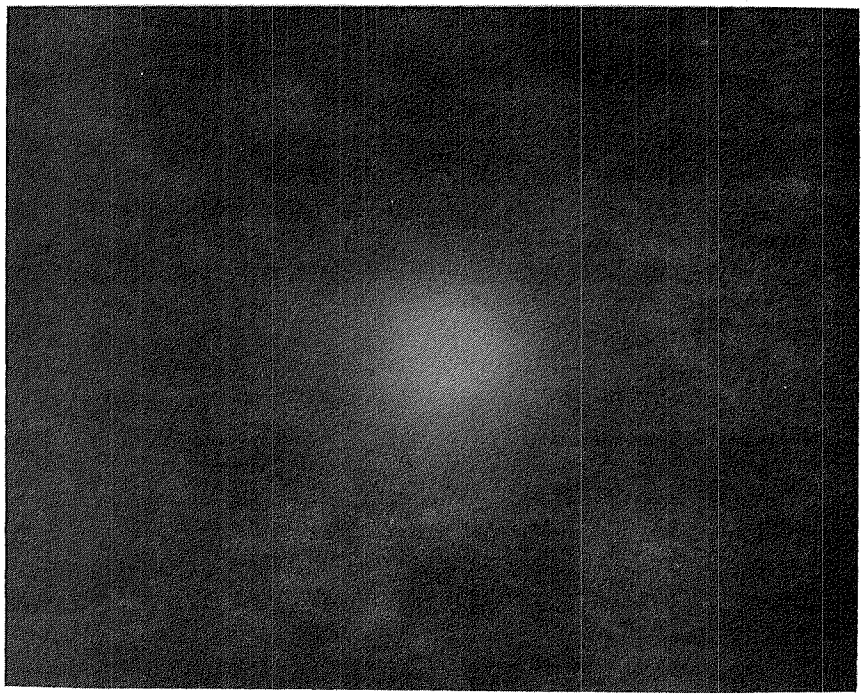


Figure 5. - Transmission electron diffraction pattern of carbon film.

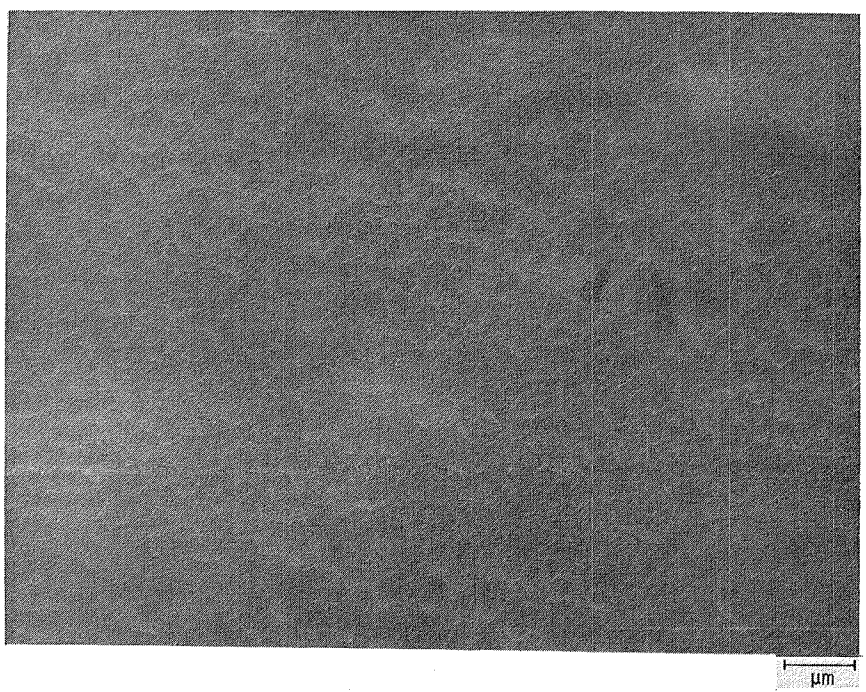
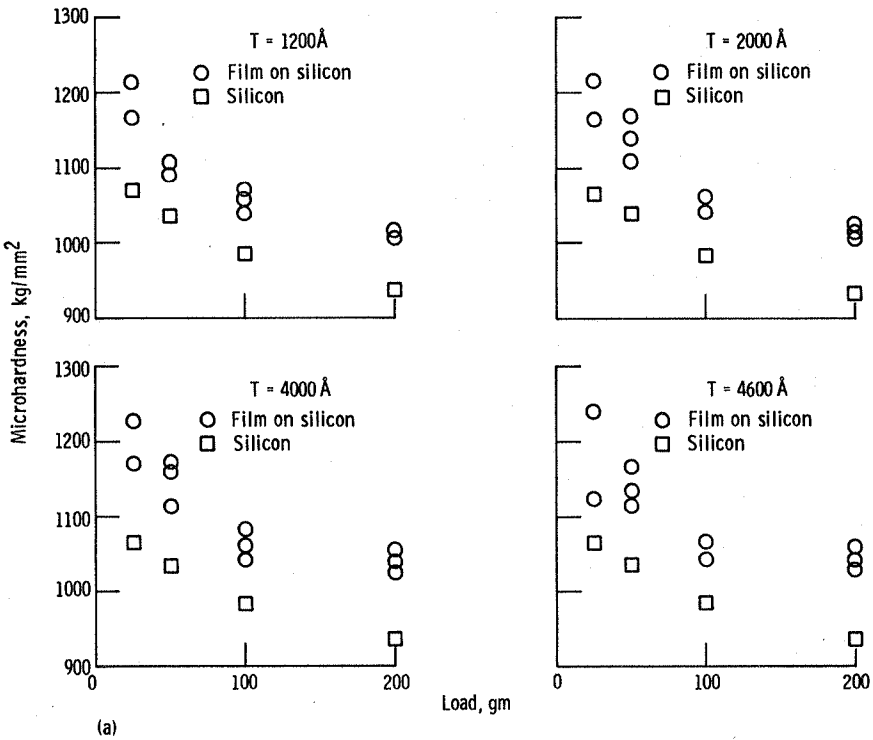
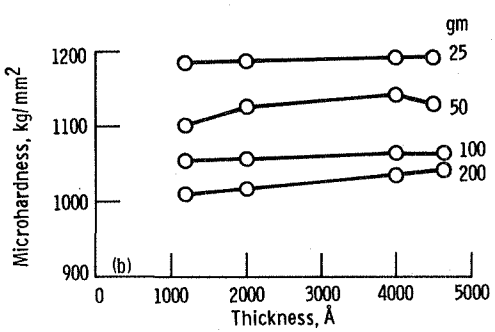


Figure 6. - Scanning electron photo-micrograph of carbon film surface.





(a) Microhardness vs load for several values of thickness (T).

(b) Microhardness vs thickness for several values of load.

Figure 7. - Microhardness as a function of load and thickness.

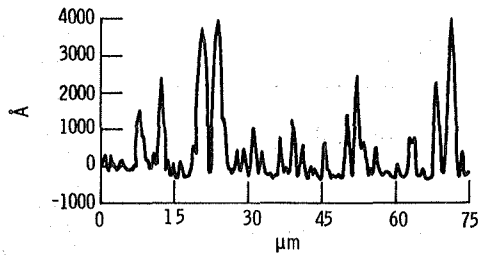


Figure 8. - Surface profile of vacuum arc film showing inclusions.

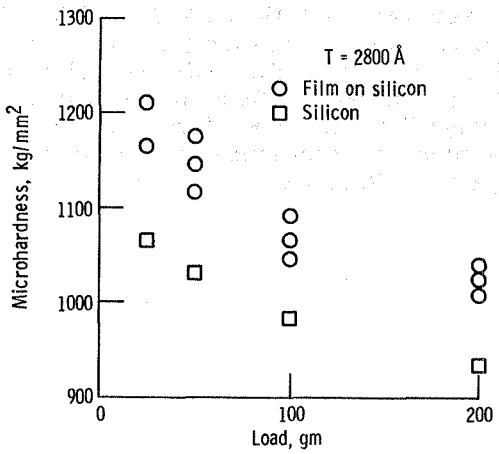


Figure 9. - Microhardness vs load for typical vacuum arc film.

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15. Supplementary Notes

16. Abstract

A program to grow thin carbon films and investigate their physical and electrical properties has been started at NASA Lewis Research Center. This paper presents characteristics of films grown by rf sputtering and vacuum arc-deposition on p-type, (100) silicon wafers. Microhardness data were obtained from both the films and the silicon via the Vickers diamond indentation technique. These data show that the films are always harder than the silicon, even when the films are thin (of the order of 1000 A). Vacuum arc films were found to contain black carbon inclusions of the order of a few microns in size, and clusters of inclusions of the order of tens of microns. Transmission electron diffraction showed that the films being studied were amorphous in structure.

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