Influence of hydrogen on the thermomechanical properties of a-CN$_x$:H and a-CN$_x$ films deposited by glow discharge and ion beam assisted deposition

A. Champi *, P.F. Barbieri, F.C. Marques

Physics Institute 'Gleb Wathagin', State University at Campinas (UNICAMP), Cidade Universitária Zeferino Vaz-GPOMS/DEQ/IFGW, Barão Geraldo, 13083970-Campinas, Caixa-Postal: 6165 SP, Brazil

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Abstract

The coefficient of thermal expansion (CTE), Young’s modulus, Poisson’s ratio, stress and hardness of a-CN$_x$ and a-CN$_x$:H were investigated as a function of nitrogen concentration. Hydrogenated films were prepared by glow discharge, GD, and unhydrogenated films were prepared by ion beam assisted deposition, IBAD. Using nanohardness measurements and the thermally induced bending technique, it was possible to extract separately, Young’s modulus and Poisson’s ratio. A strong influence of hydrogen, in a-CN$_x$:H films, was observed on the CTE, which reaches about $9 \times 10^{-6}$ C$^{-1}$, close to that of graphite ($8 \times 10^{-6}$ C$^{-1}$) for nitrogen concentration as low as 5 at.%. On the other hand, the CTE of unhydrogenated films increases with nitrogen concentration at a much lower rate, reaching $5.5 \times 10^{-6}$ C$^{-1}$ for 33 at.% nitrogen.

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1. Introduction

Carbon–nitrogen films have been intensively investigated due to the theoretically predicted super hard compound β-C$_3$N$_4$ [1]. Several works have been performed trying the development of its amorphous counterpart, a-C$_3$N$_4$, aiming to achieve very hard amorphous films [2,3]. Potential applications of amorphous carbon films and alloys [4,5] require their use at temperatures different from the deposition temperature. Thus, thermal stress appears as a result of the difference between the coefficient of thermal expansion (CTE) of the film and the substrate. However, in spite of the interest in these properties, there are few data reported in the literature concerning the CTE, and other thermomechanical properties of thin films of amorphous carbon and alloys [6,7]. In this paper, we present a study of the behavior of some thermomechanical properties, such as the CTE, Young’s modulus, Poisson’s ratio, stress and hardness as a function of nitrogen concentration using two different deposition system to obtain hydrogenated (a-CN$_x$:H) and unhydrogenated (a-CN$_x$) amorphous carbon–nitrogen films.

2. Experimental

Two series of a-C:H:N$_x$ films were prepared by glow discharge under two different bias voltage $-200$ and $-800$ V.
The films were deposited at room temperature in a gas mixture of methane $\text{CH}_4$ and $\text{N}_2$. The nitrogen partial pressure was varied in order to change the nitrogen concentration, but the total pressure was kept constant at 1 Pa. The films prepared at $-800 \text{ V}$ are more graphite-like, while those prepared at $-200 \text{ V}$ are more diamond-like. For more details on the deposition condition and other properties, see Ref. [8]. On the other hand, unhydrogenated a-C:N$_x$ films were prepared by ion beam assisted deposition with nitrogen concentration ranging from 0 at.% to $\sim 33 \text{ at.}%$. A Kaufman ion source was used to bombard a graphite target with an argon ion beam of 1500 eV, and a second Kaufman source was used to bombard the film with nitrogen ions, with a current varying in the 0.6–4.0 A range. More details on the used system, deposition condition and on some optical and structural properties of films prepared under the same condition can be found in Ref. [9]. X-ray photoelectron spectroscopy and nuclear reaction analysis were used to determine the nitrogen content. The thermally induced bending technique [10] and nanoindentation were used to determine the CTE, stress, Young’s modulus and Poisson’s ratio.

3. Results

Fig. 1 shows the CTE of a-C:H:N$_x$ and a-C:N$_x$ films as a function of the nitrogen concentration. We can observe that the CTE increases significantly in the two series of films prepared by glow discharge, reaching $\sim 9 \times 10^{-6} \text{ C}^{-1}$ for nitrogen concentration of only 5 at.%. On the other hand, the thermal expansion increases at a much lower rate for the series of unhydrogenated films, reaching $5.5 \times 10^{-6} \text{ C}^{-1}$ for nitrogen concentration of 33 at.%.

Fig. 2 displays Young’s modulus ($E$) and Poisson’s ratio ($\nu$) as a function of the nitrogen concentration. Both parameters decrease as the nitrogen concentration increases in the low concentration range. However, the unhydrogenated series presents an odd behavior with Young’s modulus and Poisson’s ratio presenting some change in the behavior at about 20 at.% nitrogen. The hardness and stress of the films follow a very similar behavior (see Fig. 3).

Fig. 1. Coefficient of thermal expansion (CTE) of a-C:H:N$_x$ and a-C:N$_x$ films as a function of nitrogen concentration.

Fig. 2. (A) Young’s modulus $E$, and (B) Poisson’s ratio $\nu$ as a function of nitrogen concentration of a-C:N$_x$ and a-C:H:N$_x$ films.

Fig. 3. (A) Hardness and (B) intrinsic stress as a function of nitrogen concentration of a-C:N$_x$ and a-C:H:N$_x$ films.
4. Discussion

The CTEs of the two series of a-CN_x:H films prepared by glow discharge are not much different from each other, except for pure amorphous hydrogenated carbon, a-C:H. In this case, the CTE of the series prepared at −200 V is close to that of crystalline diamond (1 × 10^{-6} \text{ C}^{-1}). In fact, a-C:H prepared at this bias tend to be more diamond-like (high concentration of sp^3 sites), while films prepared at high bias tend to be more graphite-like (high concentration of sp^2 sites).

As it was observed in Fig. 1, the thermal expansion of the three series of films increases with nitrogen concentration. However, the increment for the hydrogenated films is much abrupt than that for unhydrogenated films. The explanation of this behavior is likely to be related to the presence of hydrogen, since it is the only difference between the two series of films, considering their composition. Hydrogen atoms bonded to nitrogen is a terminal bond, leaving the other two nitrogen bonds free. Thus, one possible scenario is that where such nitrogen atoms work as a bridge between graphite clusters. Through this process a percolation of graphite cluster could be obtained, resulting in an increase in the thermal expansion coefficient toward that of graphite, which is about 8 × 10^{-6} \text{ C}^{-1} \text{ [11]}. As it is well known, the CTE is mainly determined by the skeleton structure of the material. For instance, the CTE does not change if one introduces holes in the material, even though Young’s modulus and hardness may change significantly. A percolation of graphite cluster may play this role, forming a structure controlled by the graphite cluster.

By this way, it would not be necessary to claim an increase in the cluster size to explain an increase in the CTE. In the case of the unhydrogenated films, the percolation would not be as easy, since the three nitrogen bonds are strongly bonded to carbon atoms. Thus, the replacement of C–C bonds to C–N bonds, as the nitrogen concentration increases, may be the main reason for the increase in the CTE of the a-CN_x films.

It was observed in Figs. 2 and 3 that the behavior of the elastic properties, stress and hardness, as a function of nitrogen, present some structure around 20 at.% nitrogen. This behavior must be related to the structure of these particular series of films prepared by IBAD. Ref. [9] presents several other properties of films prepared under the same condition, showing an anomalously behavior around 20 at.% nitrogen. This behavior has not been observed in other carbon–nitrogen alloys prepared by other techniques. Thus, it seems to be related to this particular technique, IBAD. Considering the results reported in Ref. [9], one would also expect some similarity concerning to other properties such as Young’s modulus, Poisson’s ratio, Hardness and stress, as observed in Figs. 2 and 3.

The high hardness of the films with about 20 at.% nitrogen (Fig. 3) is in fact related to elastic recovery, see Ref. [9]. In fact, Young’s modulus (Fig. 2) has the opposite behavior, being smaller around this concentration, consistent with the increase in the elastic recovery in the same range.

5. Conclusions

Thermomechanical properties of amorphous hydrogenated and unhydrogenated carbon–nitrogen alloys were investigated. The behavior of Young’s modulus, Poisson’s ratio, stress and hardness was associated with nitrogen concentration and the presence of hydrogen into the film structure. The thermal expansion is strongly affected by hydrogen, which is likely acting as a percolating agent between graphite clusters.

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References