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Insertion of nanocrystalline diamond film and the addition of hydrogen gas during deposition for adhesion improvement of cubic boron nitride thin film deposited by unbalanced magnetron sputtering method

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ABSTRACT

Cubic boron nitride (c-BN) thick film growth was attempted by the addition of hydrogen for residual stress reduction and by using a nanocrystalline diamond (NCD) buffer layer for stabilizing the turbostratic boron nitride interfacial layer. The c-BN films were deposited by the unbalanced magnetron sputtering method. Thin (100 μm) Si strips (3 × 40 mm^2) were used as substrates. A boron nitride target was used, which was connected to a radio frequency power supply at 400 W. High frequency power connected to a substrate holder was used for self-biasing of −40 V. The deposition pressure was 0.27 Pa with a flow of Ar (18 sccm)–N_2 (2 sccm) mixed gas. Hydrogen gas of 2 sccm was added to the Ar–N_2 mixed gas. The effect of the addition time of the hydrogen to the Ar–N_2 gas during deposition was investigated and found to be critical to the occurrence of the delamination of the c-BN film on the NCD buffer layer. As the addition of the hydrogen was delayed, the delamination started later. C-BN film of 3 μm thickness adherent to the substrate was obtained.

1. Introduction

Since it possesses marked mechanical properties such as hardness, oxidation resistance, and chemical inertness to ferrous metals at high temperatures, cubic boron nitride (c-BN) thin film is considered as a good candidate for next generation coating materials for cutting tools. A few results have been reported on the cutting performance of c-BN coated tools [1], but it has yet to be used commercially in industrial fields. One of the great hurdles that prevent its practical use is weak adhesion at the interface between the c-BN film and the substrate.

The weak adhesion of c-BN films is caused by high compressive residual stress of the film and low mechanical strength, as well as reactivity with the moisture of the interfacial turbostratic BN (t-BN) layer. Recently we reported that the compressive residual stress could be reduced down to less than 2 GPa by the addition of hydrogen to the sputtering gas [2,3]. Even though the residual stress was thus reduced to a meaningful value for the application as proposed by Ulrich et al. [4], the films maintained their c-BN fraction still above 60%. In addition to this, it is reported that the instability of the interfacial t-BN layer could be enhanced by using a nanocrystalline diamond (NCD) film prior to depositing the BN film [5]. Even though no epitaxial growth of the c-BN film on the NCD was observed in the previous report [5], the adhesion improvement on the NCD film was obvious. In this paper, we tried to enhance the adhesion of c-BN film and to grow films thicker than 1 μm by combining these two effects.

2. Experimental details

NCD film of about 300 nm thick with the grain size of 10–15 nm was deposited on a Si substrate by the hot filament chemical vapor deposition method. Experimental details were well described in a paper written by Li et al. [6].

BN films were deposited on the NCD coated substrate. In order to measure residual stress by the bending method [7–9], we used a thin Si substrate of 100 μm thick with the NCD buffer layer on it. The substrate remained flat after the deposition of the NCD layer, due to zero residual stress of the NCD film. The substrate was cut into a long strip with the dimensions of 3 × 40 mm^2. Films were deposited using the unbalanced magnetron sputtering method. A hexagonal boron nitride (h-BN) disk of 50 mm in diameter (99.5% in purity) was used as a sputter target. The sputter target and the substrate were connected to 13.56 MHz radio frequency electric power at 400 W and high-frequency (200 kHz) electric power for self-biasing at −40 V to the substrate, respectively. The chamber was evacuated to less than 1.3×10^{-4} Pa and then maintained at a pressure of 0.27 Pa with a flow of Ar–N_2 mixed gas. The flow rates of argon and nitrogen were 18 and 2 sccm, respectively.

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Hydrogen was added to the argon–nitrogen mixed gas with a flow rate at 2 sccm. Considering the possible reaction of hydrogen on the NCD surface and to prohibit it, we endeavored to add the hydrogen to the Ar–N_2 mixed gas at 1, 3, 5, 10 and 15 min after the start of the deposition like a schematic diagram shown in Fig. 1. The deposition time was fixed at 20 min. The films had a similar thickness of 119 nm ± 11 nm, irrespective of the hydrogen addition time. The target was pre-sputtered for 5 min before deposition with the shutter closed. The distance between the target and the substrate was 75 mm. During the deposition process, we didn't use additional heating of the substrate.

The lattice structure and crystal quality were analyzed using Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer Frontier FTIR) in the transmission mode with a resolution of 4 cm^{-1}. The spectrum of a clean silicon wafer with NCD buffer layer was taken as a background and ratioed from measured spectra of deposited films. The thickness of the films was measured on cross-section image of the films using scanning electron microscopy operated at 15 kV (Hitachi S 4200). Residual stress was calculated by Stoney equation using curvatures of a strip of 0.1 mm thick and 3 mm × 40 mm dimension measured by a beam bending method during deposition.

3. Results and discussion

Stress variation of the c-BN films deposited on a NCD layer with and without hydrogen addition was compared. The c-BN contents of the two films were measured from their FTIR spectra to be similar value of about 80%, within an error range. Fig. 2 shows the residual stress variation of the thin strip with the thickness of the film in the case of with and without hydrogen addition. The residual stress, estimated from the curvature value, is reduced remarkably with the addition of hydrogen. This is in accordance with the result reported previously [2,3]. This shows that the insertion of the NCD buffer layer between the Si substrate and the BN film showed little influence on the effect of hydrogen on the residual stress reduction of BN films.

The films deposited on the NCD buffer layer, however, delaminated promptly after the exposure to atmosphere in the case of the hydrogen addition while those without the hydrogen maintained their adherence for more than 1 day. Fig. 3 shows examples of the film's surface observed after being exposed to the atmosphere. The films deposited on the bare Si substrate were shown to be very adherent while those deposited on the NCD buffer layer delaminated promptly after exposure to the atmosphere. Despite the low residual stress of the film due to the hydrogen effect, the prompt delamination of the film indicates the possibility of another cause for delamination other than residual stress. The BN film deposited on the NCD film also consisted of amorphous BN/t-BN/c-BN 3 layers, as reported previously [5] and the film on the NCD layer was reported to be more stable under moisture than that deposited on the bare Si substrate. It is, thus, concluded that such delamination was caused by an adverse effect of hydrogen, which weakens interfaces under ambient atmosphere. The fact of the prompt delamination after the exposure offers a possibility that the delamination is related with the reaction occurring at the interface. The interface between the BN film and the Si substrate is substituted with the interface between the Si and NCD and the interface between the NCD and the BN phase. The interface between the Si and the NCD is believed to be stable under the atmospheric condition; this is because no delamination has been observed during the sample preparation stage of the NCD coated Si substrate. The interface between the NCD and the BN film is a possible site for the delamination, which was observed in a cross-sectional image of SEM. The existence of the hydrogen can change the lattice structure of the NCD surface, since hydrogen is an element that forms sp^3 bonding on the surface of the NCD layer.

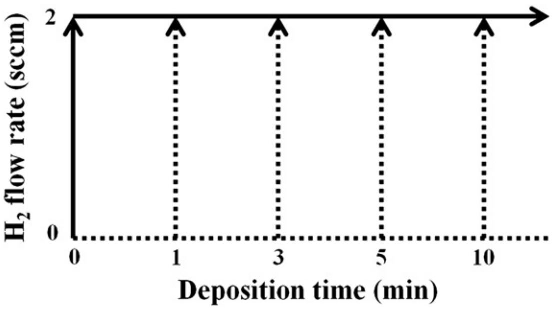

Fig. 1. Variation of the compressive stress of thin strip with thickness, with BN film deposited on it with or without hydrogen addition (NCD buffer layer was used).

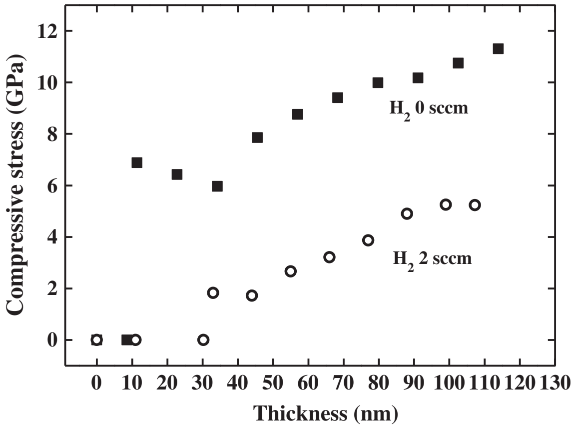

Fig. 2. Surface morphologies of BN films on NCD buffer layer deposited (a) without and (b) with hydrogen addition.

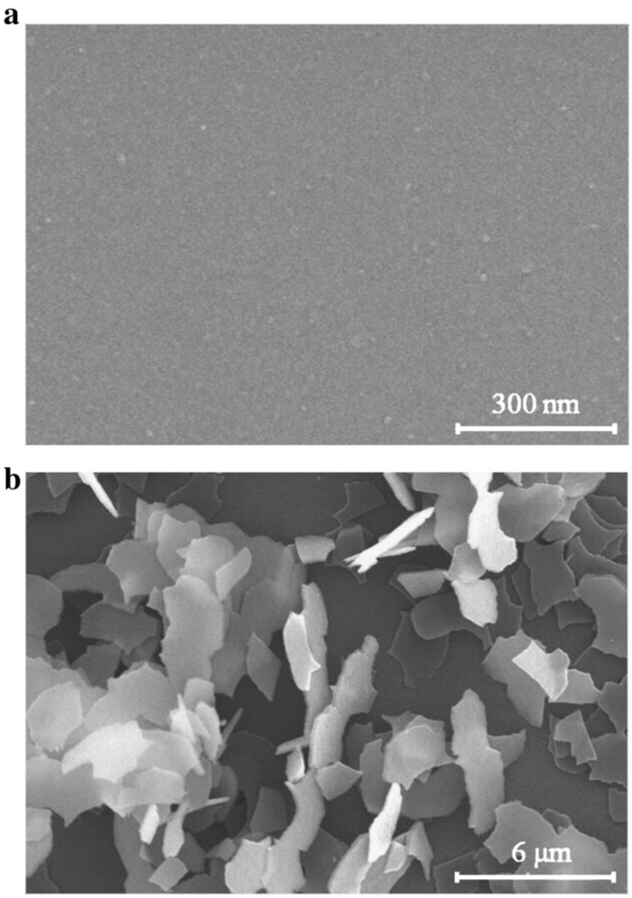

Fig. 3. Modified deposition process diagram for hydrogen addition.