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Wafer bowing control of free-standing heteroepitaxial diamond (100) films grown on Ir(100) substrates via patterned nucleation growth

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ABSTRACT

The potential of patterned nucleation growth (PNG) technique to control the wafer bowing of free-standing heteroepitaxial diamond films was investigated. The heteroepitaxial diamond (100) films were grown on an Ir(100) substrate via PNG technique with different patterns of nucleation regions (NRs), which were dot-arrays with 8 or 13 μm pitch aligned to <100> or <110> direction of the Ir(100) substrate. The wafer bows and the local stress distributions of the free-standing films were measured using a confocal micro-Raman spectrometer. For each NR pattern, the stress evolutions within the early stage of diamond growth were also studied together with a scanning electron microscopic observation of the coalescing diamond particles. These investigations revealed that the NR pattern, in terms of pitch and direction of dot-array, strongly affects the compressive stress on the nucleation side of the diamond film and dominantly contributes to the elastic deformation of the free-standing film. This indicates that the PNG technique with an appropriate NR pattern is a promising solution to fabricate free-standing heteroepitaxial diamond films with extremely small bows.

1. Introduction

Single crystalline diamond films are known to be excellent materials for a variety of optical and electronic applications owing to their extreme properties such as high optical transparency, high Young's modulus, high thermal conductivity, high carrier transport speeds, and high breakdown field. For industrial applications of diamond films, a reproducible fabrication technique of large size and high quality diamond wafers is required. One of the most promising techniques to fabricate large size diamond wafers is chemical vapor deposition (CVD). Most of the efforts have been made for homoepitaxial CVD on high temperature and high pressure single crystalline diamond substrates because of its potential of high quality [1]. On the other hand, heteroepitaxial CVD of diamond has the demerit of low quality as it stands but has the merit of possible size enlargement and cost reduction. Therefore, the development of a growth technique of heteroepitaxial diamond films is highly desired for any diamond based industrial applications.

A large number of attempts have been made to produce highly oriented heteroepitaxial diamond films on various substrate materials, for example, c-BN, Ni, Si, β-SiC, Co, Pt, and Ir. So far the highest quality of heteroepitaxial diamond film, showing the narrowest full width at half maximum (FWHM) of both the diamond (004) X-ray rocking curve and the first-order diamond Raman scattering peak, is grown on Ir(100) substrate [2,3]. However, the fabrication of large size heteroepitaxial diamond films on Ir substrates has been technically hampered by the inherent mismatch problems of lattice constant and thermal expansion coefficient between the diamond film and the substrate. One of the most critical issues derived from such mismatch problems is that the free-standing diamond films separated from the substrate have a rather large bow, which makes subsequent processes, such as polishing and bonding, difficult or even impossible. In this context, patterned nucleation growth (PNG) is a promising technique to cope with the unwanted effects derived from the mismatch problems because the contact area between diamond films and substrates can be reduced within the circumscribed nucleation regions (NRs) in a desired form. This makes epitaxial diamond crystals to grow laterally over non-nucleated Ir substrate surfaces and subsequently coalesce with each other. Using this technique, in reality, the separation of epitaxial diamond films from the Ir substrates is rather easily performed because the laterally overgrown films are not strongly adhered to the substrates [4]. More importantly, this technique allows to significantly reduce the bow of the free-standing diamond films and its direction can be even opposite from that of conventional (without PNG) epitaxial diamond films grown on Ir substrate [4]. Furthermore, the crystalline quality, in

Abbreviations: PNG, patterned nucleation growth; NR, nucleation region; CVD, chemical vapor deposition; FWHM, full width at half maximum; TEC, thermal expansion coefficient; RT, room temperature.

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terms of crystal orientation and dislocation density, can be improved via the method of epitaxial lateral overgrowth combined with PNG [5,6]. These advantages indicate the high potential of PNG technique for the fabrication of larger size and higher quality free-standing heteroepitaxial diamond films. However, the influence of PNG technique on the wafer bowing of free-standing heteroepitaxial diamond films has not been fully understood since no systematic study concerning the wafer bow variation originated from NR patterns has been performed. In this work, the influence of NR patterns on the wafer bow variation of free-standing heteroepitaxial diamond films is systematically studied. Further, the local stress distributions of diamond films grown via different NR patterns of PNG are analyzed to understand the physics behind the bow change. These investigations finally show a great potential of PNG technique to control the intrinsic wafer bow of free-standing heteroepitaxial diamond films.

2. Experimental details

The substrate used in this work was a heteroepitaxial Ir(001) film of approximately 400 nm thick deposited on a MgO(001) plate ($10 \times 10 \times 0.5$ mm^3) by sputtering. The temperature of the MgO(001) plate was kept at 953 K during the Ir sputtering. Ion irradiation (BEN (bias enhanced nucleation) in general) as an epitaxial diamond nucleation treatment [2] was carried out to the Ir surface using CH_4/H_2 gas with dc discharge. The conditions of the ion irradiation are summarized in the first column of Table 1.

For PNG, four types of resist mask patterns were formed on the ion-irradiated Ir surface by electron beam lithography. The resist mask patterns are shown in Fig. 1 schematically. As shown in Fig. 1a), four circular NRs (2 mm in diameter) with two types of dot-pitches and dot-directions were made on the same substrate to eliminate the influence of subtle changes in growth conditions if they were grown on different substrates. Within the circular NRs, circular dots of resist masks with a diameter of 3 μm were aligned at a pitch of 8 or 13 μm along <100> or <110> direction of Ir(100) substrate as shown in Fig. 1b). The dot diameter of 3 μm was chosen in order to obtain sufficient numbers (~700) of diamond nuclei inside the dots since the nucleus density is an important issue for the successful heteroepitaxial diamond growth [7]. The masked substrate was treated by neutralized Ar beam for 130 s to bombard the un-masked areas so as not to have a diamond growth. The etching conditions are summarized in the second column of Table 1 except for the incident beam angle from the sample surface normal of 0°. Then, epitaxial diamond films were grown on the resulting Ir surface in a dc-plasma CVD chamber at a constant substrate temperature of 1300 K. Two types of growth conditions were chosen; one was a short-time (20, 40, 60, 80, 100, 120, 140, and 160 min) growth of micro-sized epitaxial diamond particles and further continuous films, and another was a long-time (5 h) growth for the fabrication of approximately 75 μm thick free-standing diamond films. The growth conditions are summarized in the third column of Table 1. For a comparison, an ~75 μm thick diamond film was conventionally grown (without using PNG technique) with the long-time growth condition. All the diamond films fabricated with the long-time

Table 1
Conditions of ion irradiation, Ar beam etching, and diamond growth.

	BEN	Ar beam etching	Diamond growth
CH_4/H_2 ratio	2 %		5 %
Gas pressure	15.3 kPa	4.7×10^{-2} Pa	16 kPa
Accelerating/bias voltage	~400 V	~500 V	
Discharge current density	~2 kA/m^2	~10 A/m^2	~18 kA/m^2
Substrate temperature	1210 K		1300 K
Duration	90 s	130 s/50 h	20~160 min, 5 h

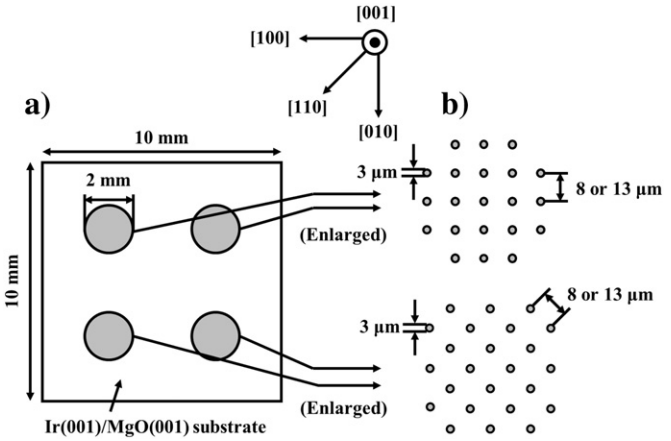

Fig. 1. Schematic illustration of dot-shaped resist mask patterns arranged with 8 or 13 μm pitch along <100> or <110> direction placed on Ir(001)/MgO(001) substrate separately. a) Macroscopic view and b) enlarged view.

growth condition were essentially peeled off from the Ir/MgO substrate after the growth. In order to completely remove the small parts of remaining Ir/MgO from the nucleation sides of the diamond films, the long-time growth samples were subsequently treated as follows. The samples were treated with 60% nitric acid at about 473 K for 40 min to remove the MgO back-plate. Then, the samples were heated up to ~673 K after pasting eutectic Pb–Sn solder on the back-side Ir. The samples were finally soaked in a mixed acid (60% nitric acid:95% sulfuric acid = 1:3) at ~473 K for 40 min. These procedures fully removed the back-side Ir/MgO and completely formed free-standing diamond films with a diameter of 2 mm. All the samples made in this study (37 in total) are summarized in Table 2 with the defined sample names, for example, coalescing film_P8<100>20 m.

The surface morphologies of coalescing films and free-standing films were observed by scanning electron microscopy (JEOL JSM5600) with an acceleration voltage of 20 kV. The crystal orientations of free-standing films were evaluated by a X-ray diffractometer (PANalytical X'Pert^3 MRD) configured with a copper source, providing X-rays with a wavelength of 1.54 Å, and 4-bounce Ge(022) monochromator. The profiles (deflections) of both the growth sides and the nucleation sides of the films were measured using an auto-tracking capability of the confocal incident light (532 nm) beam of a commercial Raman scattering apparatus (Renishaw inVia Reflex) with a spatial resolution of ~0.5 μm. In the auto-tracking measurement, the top position of the sample is automatically determined by searching the brightest laser light reflected from the sample surface using an equipped CCD camera. Since the areas closer to film edges tend to have a faster growth speed of diamond due to the higher concentration of CVD plasma toward the film edges (the difference of growth speed on the films is below about 13% in the case of present samples), the bows of the nucleation sides were defined as the real bows of the films. The bows were rotationally nearly-symmetric convex–concave shapes with a concave side on the nucleation side.

The relative internal stresses of coalescing films and free-standing films were evaluated by the wave number shifts of Raman scattering peaks (first-order Raman peaks of diamond) which were always referenced to the Raman scattering peak of a commercial HPHT Ib (001) diamond (Sumitomo Electric Industries, Ltd.). The wave number of the Raman scattering peak of the referenced Ib diamond was adjusted to 1332.5 cm^{-1} [8,9]. Under the assumption that the stress of diamond films is isotropic, the circularly polarized excitation light was chosen to estimate the hydrostatic stresses of the present samples since the hydrostatic stress values can be approximately estimated from the first-order diamond Raman peaks [10]. Position (both lateral and depth directions) dependences of