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Simultaneous formation of nanocrystalline and <100> textured and {111} facet dominated microcrystalline diamond films using $CH_4/H_2/O_2$ plasma ☆

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A R T I C L E I N F O

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A B S T R A C T

Here, we report on the simultaneous production of a white transparent and a gray translucent microcrystalline diamond film from one microwave plasma chemical vapor deposition (CVD) run and focus on the diamond film morphology on the lower substrate that consisted of a small square Si on a 2-inch Si wafer. The growth was performed with a 0.38% O_2 addition into 4% CH_4/H_2 gas mixture under microwave power 3200 W. Besides the {111} facet dominant morphology, a local gradient morphology is also formed on the lower 2-inch Si wafer in a narrow region surrounding where the upper small square Si was placed. It consists of a narrow gradual morphology transition from nanocrystalline diamond grains through {100} facetted gradually towards a {111} facet dominated feature. In particular, the shining narrow square belt on the centre of 2-inch Si wafer is composed by smooth {100} facets. Based on the relationship between the growth conditions and the diamond film morphologies, we can analyze the impact of the presence of the upper small square Si substrate on the formation of {100} faceted diamond and the uniformity of diamond growth on the lower 2-inch Si wafer. By comparing the present results with our previous experimental work on nitrogen addition, we can deduce that the effect of oxygen addition on diamond growth is not very sensitive to temperature variation and opposite to the role of nitrogen addition. These results can serve as experimental validation for the simulation of the plasma distribution under high power conditions.

1. Introduction

Butler et al. have reviewed the recent progress on the understanding of the chemical vapour deposition (CVD) of diamond materials with a particular focus on the commonly used microwave plasma activated CVD (MPCVD), because it has become dominant in both industrial and research facilities worldwide [1]. The basic understanding of diamond growth using hydrogen/hydrocarbon chemistry, the so-called "standard growth mechanism" developed in the early 1990s [2], deals with a typical gas mixture using a few percentages of CH_4 in H_2, the 'standard model' of diamond CVD. A detailed understanding of the many parameters affecting growth, for example microwave power, the substrate temperature, gas mixture, process pressure, is required in order to obtain a diamond film with the desired morphology combined with controlled optical, electronic and mechanical properties [3].

A small amount addition of nitrogen, oxygen to the standard CH_4/H_2 gas mixture and depending upon the growth conditions, substrate properties and growth time, can produce polycrystalline diamond films with grain sizes from nanometer scale to millimetres [4,5]. Although the effects of nitrogen and oxygen addition to the CH_4/H_2 gas on the diamond film morphology has been intensively studied in the 90s [6], and the role of oxygen, nitrogen can be viewed as a perturbation of the hydrogen/hydrocarbon chemistries; however, even 20 years after diamond CVD was first developed, the detailed effects of nitrogen, oxygen addition under different growth conditions especially for high power MPCVD systems have not yet fully explored by experiments and the exact details of the growth mechanism remain controversial, and thus a comprehensive understanding of the MPCVD diamond process has not yet achieved.

In high power (≥3 kW) MPCVD systems, the substrate is directly heated by the plasma and the substrate holder is generally water cooled by a closed cycle [7]. Therefore, higher substrate temperatures are usually tuned by increasing the microwave power. Alternatively, without changing microwave power, it is still possible to obtain high and low substrate temperatures on different Si substrates of various sizes in one deposition run using a high-power MPCVD reactor by placing a small square Si piece usually of 1 cm^2 area centrally on a 2-inch Si wafer [8,9]. For example, using this method, we have simultaneously produced cauliflower-like nanocrystalline diamond (NCD) on the lower 2-inch Si wafer and {100} textured microcrystalline diamond (MCD) film of large grain size about 100 μm on the small square substrate from one deposition run through 1 SCCM air induction and microwave power

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3200 W [8]. As a confirmation, similar results were also obtained with 1 SCCM pure N_2 addition and microwave power 3000 W [9].

In contrast, when only a small amount of pure O_2 (instead of nitrogen addition) was introduced while using otherwise identical growth parameters as that with nitrogen addition in Ref. [9], we have obtained only MCD films of large grain size on the major area of both silicon substrates from the same deposition run. Interestingly, a shining narrow square belt can be seen on the 2-inch Si wafer surrounding where the small square Si was placed and it consists of smooth {100} facets. {100} facet terminated or {100} textured diamond is strongly desired for many applications due to the intrinsically smooth, flat square crystalline surface and low defect densities, and thus it has long been a focus of both experimental [10–13] and theoretical studies [14]. However, so far, the achievement of {100} textured diamond or highly oriented diamond (HOD) film was obtained either through bias enhanced nucleation (BEN) process [15] or induced by nitrogen addition [16]. Distinct from the above mentioned methods, the formation of {100} facet in this particular configuration with O_2 addition attracted our attention. We think that further analysis of this new result may shed light into the growth mechanism of {100} faceted diamond.

On the other hand, with O_2 addition, we have also found that a local morphology transition from {111} facet dominated features through {100} facet formation to nanocrystalline diamond occurs on the lower 2-inch Si wafer in a narrow region surrounding where the small square Si was placed. In the literature, well-faceted MCD and cauliflower-like NCD deposits were grown on the same silicon substrate by forcing a microwave plasma ball generated at 1 kW microwave power to touch a silicon substrate [17]. Graded-morphology diamond thin films were prepared by using MPCVD in a single experimental run by elevating one end of the silicon substrate [18]. From this point of view, we think that the variety of morphologies on one Si substrate we obtained with O_2 addition deserves further investigation and comparison with literature work.

Therefore, in this paper, we focus on the diamond film morphology grown with O_2 addition on the substrate that consisted of a small square Si piece on 2-inch Si wafer in detail. Based on this result, we can analyze the relationship between the growth conditions and the diamond film morphologies and discuss the impact of the presence of the upper small square Si substrate on the formation of {100} faceted diamond and plasma uniformity and distribution on the lower 2-inch Si wafer. Furthermore, by comparing the effect of oxygen addition with that of nitrogen addition under otherwise identical growth conditions, the gas phase chemistry and the specific CVD diamond growth mechanism upon oxygen or nitrogen addition may be addressed.

2. Experimental

The diamond samples were grown in a 5 kW ASTeX PDS-18 MPCVD reactor using a small Si piece of $14 \times 15\ mm^2$ area and

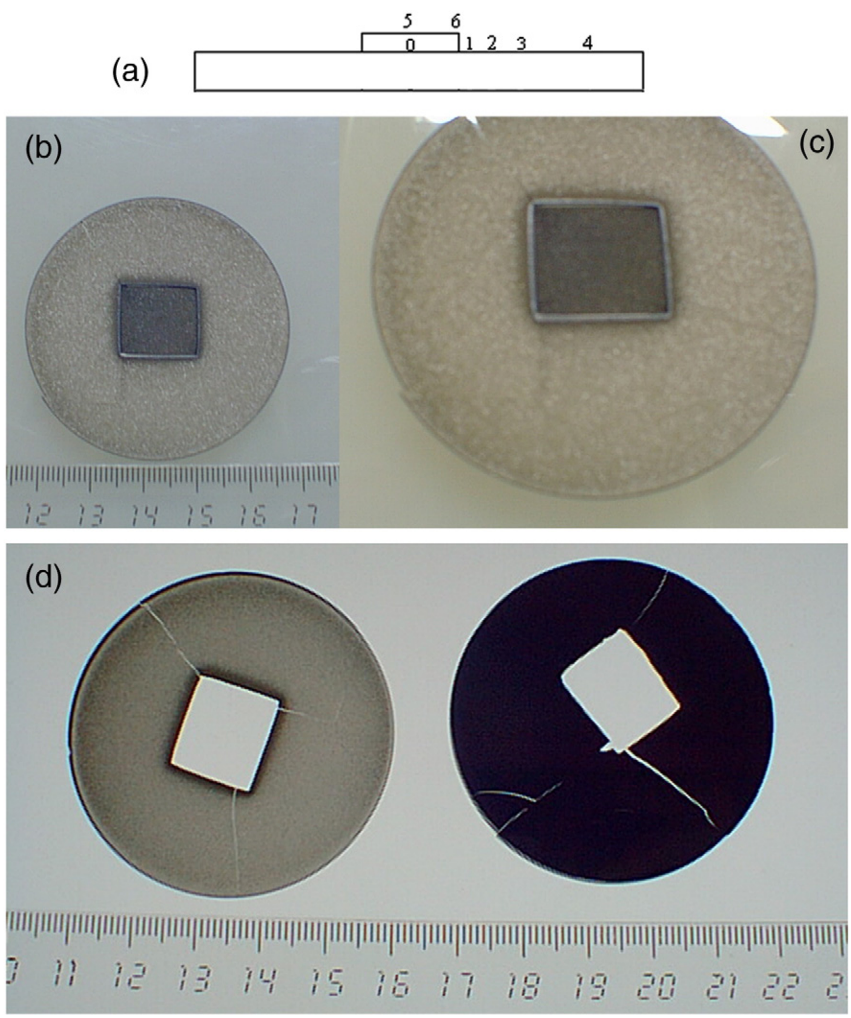

Fig. 1. Schematic of the two silicon substrate arrangement used in the present study (a), and the optical photographs of the up TD and lower BD samples: (b, c) BD and TD ($14 \times 15\ mm^2$, which is in the empty centre of sample BD), and (d) the sample BD (left) with the substrate side up together with NCD film ND1 grown with nitrogen addition (right) for comparison.