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Anisotropic evolution of damaged carbons of a mechanically polished diamond surface in low-temperature annealing

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ABSTRACT

To clarify the anisotropic evolution of damaged carbons on a mechanically polished diamond surface under low-temperature (473 K) annealing, molecular dynamics simulation is performed in this work to represent the mechanical polishing and low-temperature annealing coupled treatment on the {100} and {110} crystal planes. Coordination number, atomic density and atomic structure analyses are employed to reveal the variation laws, and a new algorithm is further developed to extract well-arranged sp^2 carbon atoms from damaged carbon atoms. The results show that more sp^2 hybridizations appear on the {110} plane after polishing, yielding a defect density of more than 1×10^{22} vac/cm^3, which is the atomic origin for the graphitization in the followed low-temperature annealing. Raman spectroscopy and electron energy loss spectroscopy analyses confirm that the graphite is only detectable on the polished {110} plane. In annealing of the polished {110} plane, graphitization is a visible evolution for the damaged carbons in the topmost surface layer, and the ordered sp^2 and sp^3 hybridizations increase monotonously. Resultantly, the atomic density of damaged surface layer decreases from 3.21 g/cm^3 to 2.47 g/cm^3, which is close to the density of graphite, 2.25 g/cm^3. On the polished {100} plane, the ordered sp^2 and sp^3 hybridizations and atomic density of damaged surface layer change hardly upon annealing. In contrast, the amorphous sp^2 phases increase considerably. In the deeper surface layer, the amorphous sp^3 carbons grow back to the tetrahedral structures at the interface between diamond cubic and ordered sp^2 structures, which has no anisotropy in annealing.

1. Introduction

As a well-known engineering material, diamond crystal has an excellent thermal conductivity, high Young's modulus and hardness, strong wear resistance and inert chemical properties. Due to such unmatched material properties, diamond crystal has been widely employed in various industrial sectors, including MEMS device, scanning probe tip, cutting tool, and so forth [1,2]. In addition, diamond crystal is a typical brittle material, and the covalent bond and tetrahedral structure of which make it only produce a minor amount of elastic deformation under a small external load. As the external load increases and exceeds a critical value, diamond surface will suffer from phase transformation, which inevitably deteriorates the mechanical properties of diamond surface [3].

In order to clarify the force-induced amorphization of diamond crystal, Grillo and Field [1] firstly explained the phase transformation from diamond cubic to amorphous sp^2 and sp^1 hybridizations as the dominant removal mechanism in mechanical polishing of diamond crystal. Gogotsi et al. [4] performed the indentation experiments on diamond surface corroborated by micro-Raman spectroscopy. They claimed that the force-induced phase transformation in diamond is inevitable, and the noncubic diamond polytypes include lonsdaleite, graphitic carbon, and possibly new phases of carbon. van Bouwelen [5] claimed that there is no elastic energy as the plastic deformation takes place in diamond crystal. In contrast, rehybridization of carbon atom takes place once the stored deformation energy of C—C bond exceeds its energy barrier, 5.5ev. Fairchild et al. [3] explored the amorphization of diamond crystal by ion implantation and molecular dynamics (MD) simulation. They found that the amorphization of diamond carbon is strain driven. When the force-induced strain in diamond reaches a critical value of 16%, the diamond lattice collapses, in which the amorphous non-diamond phases produce. Pastewka et al. [6] also employed MD simulation to represent the mechanical polishing of diamond crystal. They concluded that there is a kind of pilot-atom, which can take away the carbon atoms on the topmost surface of diamond crystal. In this case, the greater the energy of pilot-atom, the easier the carbon atoms can be taken away. Once a carbon atom departs from the lattice, the left tetrahedral structure can easily collapse. Yang

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et al. [7] found that the scratch of diamond grit inevitably facilitates the amorphization of diamond crystal in mechanical polishing. Therefore, they paid great attentions to revealing the relationship between the resistance force of diamond grit in sliding and the amorphization rate. They discovered that the greater amorphization rate appears in sliding along the soft direction because of the smaller resistance force. Zong et al. [8] also employed MD simulation to reveal the atomistic origins of the material removal rate anisotropy in mechanical polishing of diamond crystal. According to their observations, they claimed that the material removal rate is heavily dependent on the proportion of sp^2 hybridized structures to amorphous sp^3 hybridizations in the newly created surface layer and debris. The statistical results validated that the greater the proportion of sp^2 to amorphous sp^3 is in the newly created surface layer and debris, the higher the material removal rate is in polishing.

Moreover, friction and wear measurements on the diamond surface were also carried out to confirm the phase transformation at the macroscopic scale [9]. Weima et al. [10] and Roundy et al. [11] even observed the nano-degradation of diamond in the thermochemical polishing.

Therefore, previous work proved that the topmost surface layer of diamond crystal inevitably produces phase transformation in mechanical polishing, no matter what orientation of the as-polished surface [4,5]. After phase transformation, many non-diamond carbon atoms appear on the topmost surface layer of diamond crystal, which act as the lattice defects and degrade the intrinsic properties of diamond crystal [3].

In order to remove the lattice defects that introduced by phase transformation, great efforts had been tried to develop novel solutions, such as dynamic friction polishing [12] and mechanochemical polishing [13,14]. Moreover, Zong et al. proposed a new post treatment technology, namely the thermo-chemical refinement process, through which the surface hardness and Young's modulus of the diamond {110} plane polished mechanically can be improved considerably [15]. They preliminarily pointed out that the improvement of hardness and Young's modulus is attributed to the appearance of graphite in polishing, the transformation of amorphous sp^3 carbons into amorphous sp^2 carbons and graphite by annealing, and the refinement of sp^2 hybridized carbons by chemical erosion. Unfortunately, their explanation did not consider the effect of the crystal orientation. To further clarify the underlying mechanisms, low-temperature annealing treatment (at 473 K) on the mechanically polished diamond surfaces {100} and {110} is represented by MD simulation in this work. And then the anisotropic evolution of damaged carbons in annealing is explicated by the coordination number analysis, atomic density analysis and atomic structure analysis. It should be noted that the term ‘anisotropy’ in this work refers in particular to the different behaviors on the {100} and {110} surfaces.

2. Methodologies

2.1. Experiment

Firstly, two natural diamond substrates (with {100} and {110} free surfaces, respectively) were smoothened by the mechanical polishing process. Secondly, the polished diamond surface was coated by gold film to improve the electrical conductivity and protect the amorphization carbons. And then the polished diamond surface with gold deposition was observed with the transmission electron microscopy (TEM) technology to analyze the structural evolution of diamond carbons. In this step, the FEI Helios 400 s was employed to extract TEM samples from the polished diamond surface, which can provide a focused ion beam milling technology to fulfill the coarse slicing and precision thinning. In the procedure of precision thinning, Ga ions beam was operated at 5 kV and 100 pA. Thirdly, the high resolution transmission electron microscopy (HRTEM) observation was performed for the prepared samples on the FEI Talos F200X. Finally, the samples were further detected in a scanning transmission electron microscope (STEM), Titan Cubed Themis G2 300e, in which the electron energy loss spectroscopy (EELS) analysis was applied to read the different carbon phases in the damaged diamond surface layer.

Moreover, Raman spectra analysis was also conducted to confirm the different carbon phases in the damaged layer of the mechanically polished diamond surface with a confocal Raman microscope, whose laser beam has a focused spot-size of approximately 1 μm. The Raman shift increment of two adjacent sampling points was set to 0.469 cm^{-1}. In addition, the excitation wavelength of 638 nm provided by lasers operating was utilized.

2.2. Molecular dynamics modeling

In order to represent the mechanical polishing and annealing treatment along the ‘soft’ direction on the crystal planes {100} and {110} of the diamond crystal, MD simulation method was conducted in this work. As designed, the simulations were fulfilled in two steps [15]. The first step was to represent the mechanical polishing, which includes nano-indentation, nano-scratching and unloading. After the first simulation, the damaged diamond surface was achieved, on which many different amorphous carbon atoms reside. The second step was to simulate the low-temperature annealing, with which the variations of amorphous carbon atoms can be captured. MD simulation model for the mechanical polishing consists of a mono-crystalline diamond substrate (with {100} or {110} free surface) and a spherical grit, as illustrated in Fig. 1. In mechanical polishing of diamond surface, the material removal is usually regarded as an extremely thin cutting fulfilled with a large negative rake angle tool. Due to the influence of tool cutting edge radius, the diamond grit can be simplified into a sphere. The substrate

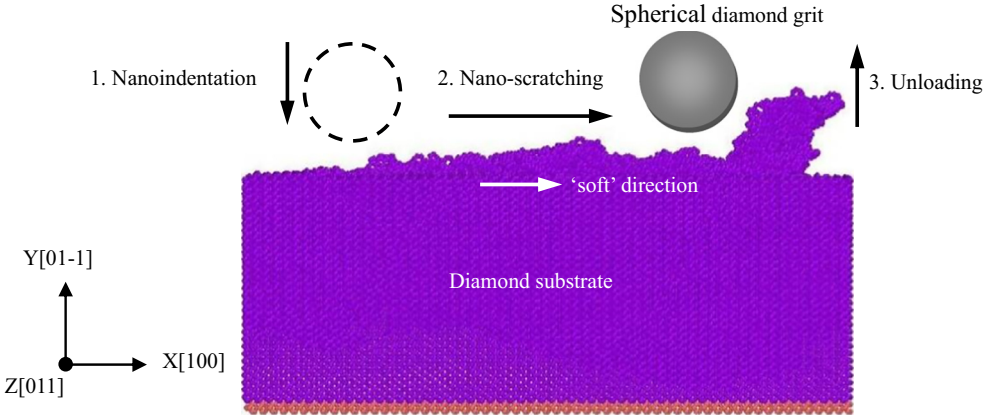

Fig. 1. Schematic illustration of MD simulation for the mechanical polishing of diamond crystal.