

Effects of microwave oxygen plasma treatments on microstructure and Ge-V photoluminescent properties of diamond particles*

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The microstructure and Ge-V photoluminescent properties of diamond particles treated by microwave oxygen plasma are investigated. The results show that in the first 5 min of microwave plasma treatment, graphite and disordered carbon on the surface of the particles are etched away, so that diamond with regular crystal plane, smaller lattice stress, and better crystal quality is exposed, producing a Ge-V photoluminescence (PL) intensity 4 times stronger and PL peak FWHM (full width at half maximum) value of 6.6 nm smaller than the as-deposited sample. It is observed that the cycles of 'diamond is converted into graphite and disordered carbon, then the graphite and disordered carbon are etched' can occur with the treatment time further increasing. During these cycles, the particle surface alternately appears smooth and rough, corresponding to the strengthening and weakening of Ge-V PL intensity, respectively, while the PL intensity is always stronger than that of the as-deposited sample. The results suggest that not only graphite but also disordered carbon weakens the Ge-V PL intensity. Our study provides a feasible way of enhancing the Ge-V PL properties and effectively controlling the surface morphology of diamond particle.

Keywords: diamond particles, Ge-V center, microwave oxygen plasma treatment, PL enhancement

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1. Introduction

Diamond crystal has a regular tetrahedral structure, and each carbon atom is connected to surrounding carbon atoms through sp^3 hybrid orbitals. This structure gives diamond many excellent properties, such as high hardness and excellent chemical stability.^[1-3] The impurity elements presented in diamond can produce photoluminescence (PL), which is called color center and can be used in many fields. For instance, single photon source in diamond has a unique application in the field of quantum information processing.^[4] Nanodiamond with bright fluorescence can be used as fluorescent label, drug carrier, diamond waveguide,^[5] *etc.* Among the more than 500 color centers of diamond, most studied are the nitrogen-vacancy (N-V) and silicon-vacancy (Si-V) color centers. However, the PL spectrum of the N-V center has large sidebands, and only 4% of the photons are concentrated on its zero-phonon line (ZPL),^[6] resulting in low photoluminescence efficiency. Although Si-V center has narrow spectral lines, its quantum efficiency is relatively low. Recently, germanium-vacancy (Ge-V) color center,^[7,8] which is stable at room temperature, high in PL intensity, narrow in emission band, and short in luminescence lifetime of 1.4 ns,^[9] has attracted more attention. The Ge-V center has a D_{3d} symmet-

rical structure similar to the Si-V center, but in contrast, Ge-V exceeds the Si-V in quantum efficiency^[10] and relaxation time.^[11] This indicates that the Ge-V center has great potential applications in quantum communication.

To realize these exciting applications, the preparation of diamond particles with strong Ge-V PL properties is a key step. At present, the methods of preparing Ge-V center in diamond include high temperature and high pressure (HPHT), microwave plasma chemical vapor deposition (MPCVD), ion implantation, and hot filament chemical vapor deposition (HFCVD). The HPHT method is mostly used to prepare bulk Ge-V contained diamond.^[12,13] By using the MPCVD method, Ge-V-containing diamond films or micron-sized diamond particles were prepared.^[14] Sedov *et al.* realized the doping of polycrystalline diamond films and single crystal diamond layers with Ge.^[15] Ge-V center structure can also be obtained by implanting Ge ions into diamond. Iwasaki *et al.* compared the formation of Ge-V centers in diamond by MPCVD and ion implantation, and they demonstrated that MPCVD leads the line widths to narrow and the peak position to slightly vary.^[16] Besides, ion implantation will cause the crystal lattice of diamond to destruct and the color center to be distributed unevenly, resulting in weak PL intensity. Our previous experiments demonstrated that we had prepared the Ge-

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V micron-sized diamond particles by using the HFCVD.^[17] However, its Ge-V PL intensity is still weak, which dramatically obstructs the further study and application of Ge-V diamond. Numerous studies have shown that when the diamond surface is H-terminated, it will have an adverse effect on the color centers PL properties.^[18,19] While if the diamond surface is C=O terminated, it is beneficial to enhancing the PL intensity of N-V^[20–22] and Si-V^[23,24] centers. Also, microwave oxygen plasma treatment can control the termination state of the diamond surface, thereby enhancing the Si-V PL intensity.^[25,26] Compared with thermal oxidation, microwave oxygen plasma treatment is mild and can be applied to the samples with different requirements by adjusting parameters.

Here in this work, we prepare the dispersed Ge-V-containing diamond particles by using the HFCVD, and treat them with microwave oxygen plasma to enhance the Ge-V PL intensity. The results show that in the initial stage of microwave oxygen plasma treatment, disordered carbon and graphite on the particle surface are etched, leaving diamond crystals with smaller lattice stress and good quality exposed on the surface, thus improving the Ge-V PL intensity. Subsequently, there is a cyclic process in which part of diamond is converted into graphite and disordered carbon, which makes the surface roughened and the Ge-V PL intensity reduced, and then the graphite and disordered carbon are etched, which makes the crystal plane regular and the Ge-V PL intensity increase with treatment time further increasing. Moreover, in the first 60 min of microwave oxygen plasma treatment, the average particle size decreases from 117 nm to 107 nm, and the proportion of particles smaller than 100 nm in size increases significantly from 30.9% to nearly 50%. Our results indicate that the graphite and disordered carbon with this content greatly weaken the Ge-V PL intensity, and affect the surface morphology and microstructure of diamond particle. The results are of great significance for broadening the applications of Ge-V diamond particles in the fields of quantum communication.

2. Experimental methods

The high purity germanium wafer was pre-sputtered by the physical vapor deposition (PVD) system. First, it was placed into acetone and ethanol in sequence, and treated ultrasonically for 20 min to remove oil stains and impurities from the surface. Then, it was blown dry with nitrogen (N₂) gas. The cleaned Ge wafer was fixed on a target base in a PVD device. Then the Ar gas was ionized and Ar ions were accelerated and bombarded the surface of the Ge wafer, so that Ge atoms on the surface became loose and the bonding force between atoms was reduced, thereby making it etched more easily. The PVD parameters were the back pressure of 3×10^{-3} Pa, argon flow rate of 25 sccm, working pressure of

0.8 Pa, temperature of 400 °C, working power of 100 W, bias voltage of -50 V, target distance of 7 cm, and deposition time of 30 min.

Prior to the HFCVD deposition, the diamond micropowder suspension was used to ultrasonically treat the PVD-treated Ge wafer for 30 min for seeding treatment. Then, the Ge wafer was placed into the hot filament chemical vapor deposition system as a substrate, with the working parameters being the hot filament power of 1600 W, the gas mixture composition of CH₃COCH₃ : H₂ = 60 : 200 sccm, growth time of 9 min and growth pressure of 1.9 kPa.

The as-deposited diamond particles were treated by using microwave oxygen plasma. The MPCVD parameters were the microwave power of 600 W, reaction pressure of 15 Torr (1 Torr = 1.33322×10^2 Pa), and the gas mixture composition of O₂:Ar = 5:95 sccm. The effects of total time of microwave oxygen plasma treatment on diamond particle morphology, phase composition and Ge-V PL properties were studied by continuous microwave oxygen plasma treatment on the same sample. Hereafter, we use MP-t0 to denote the as-deposited sample, and MP-t5, MP-t15, MP-t30, MP-t60, and MP-t120 to refer to the 5-, 15-, 30-, 60-, and 120-min microwave-treated samples, respectively.

Field emission scanning electron microscope (Nova NanoSEM450) was used to characterize the surface morphologies of samples. Raman and PL spectra were collected by Laser Raman Spectrometer (RenishawRL532C510) with an excitation wavelength of 532 nm at room temperature. Raman spectrum was used to characterize the phase transitions of samples. The acquisition time was 30 s and the used laser power was 1 mW (accounting for 5% of total laser power, 20 mW, supplied by the Rama equipment). PL spectroscopy was used to characterize the Ge-V PL properties of diamond particles. The acquisition time was 10 s and the laser power was 1 mW.

3. Results and discussion

Figure 1 shows the FESEM images of samples treated by microwave oxygen plasma for different times. The inset in the upper right corner in each panel of Fig. 1 shows the histogram of particle size distribution of the sample, and the average particle size of samples and the proportion of particles smaller than 100 nm are calculated. Figure 1 displays that the average particle size of the as-deposited sample is about 117 nm and 30.9% of the particles are smaller than 100 nm. It is indicated that we have prepared dispersed particles by HFCVD. Some particles of the as-deposited sample have obvious crystal planes, but the surface of the particles is rough.

After 5-min microwave oxygen plasma treatment, the average particle size is reduced to 113 nm, and the proportion of particles smaller than 100 nm increases to 36.7%. The

surfaces of the particles become smooth and regular crystal planes appears. Subsequently, the average particle size of sample MP-t15 and sample MP-t30 decrease slightly to 111 nm and 110 nm, and their proportions of particles smaller than 100 nm increase slightly to 37.6% and 40.9%, respectively. Some particle surfaces of sample MP-t15 and MP-t30 show irregular and rough morphology. Further increasing the microwave oxygen plasma treatment time to 60 min, the average particle size decreases to about 107 nm. The proportion of particles smaller than 100 nm of sample MP-t60 increases obviously, approaching to 50%. In the first 60 min of microwave oxygen plasma treatment, as the average particle size gradually decreases, the proportion of particles smaller than 100 nm also increases, which indicates that all particles decrease in size during microwave oxygen plasma treatment and the mi-

crowave etching rate decreases with time increasing. The particle surface of sample MP-t60 tends to be smooth again. In addition, the regular crystal planes disappear and most of the particles are spherical.

With 120-min microwave oxygen plasma treatment, the particle size remains almost unchanged and the number of particles decreases. This means that some particles disappear and the average size of larger particles decreases to 107 nm. Then, the particle surface of sample MP-t120 becomes a little rough, and the Ge substrate is also etched. From Fig. 1, we find that during the microwave oxygen plasma treatment, the surface of the particles is alternately smoothed and roughened. With the further extension of the microwave oxygen plasma treatment time, the regular crystal plane disappears and the particles become spherical.

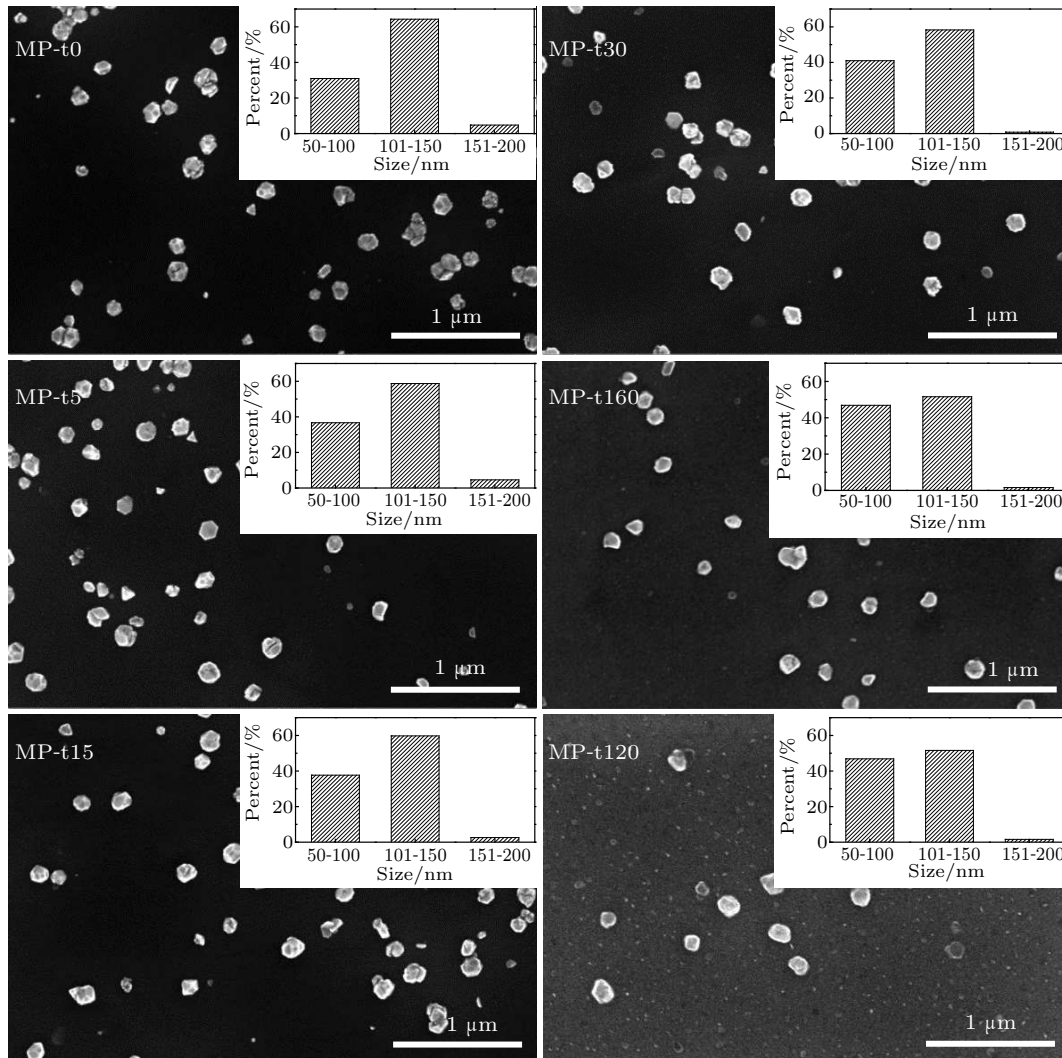


Fig. 1. FESEM images of particles treated by microwave oxygen plasma for different times with inset showing histogram of particle size distribution of each sample.

Figure 2(a) shows the PL spectra of samples treated by microwave oxygen plasma. Figures 2(b) and 2(c) show the position, FWHM values, and the normalized intensity of Ge-V PL peak versus microwave treatment time, respectively. It

is observed that the as-deposited sample MP-t0 has obvious Ge-V PL signals close to 602 nm and the FWHM of the Ge-V peak exceeding 10 nm. After 5-min microwave oxygen plasma treatment, the FWHM of the Ge-V peak significantly

decreases to 6.6 nm. The normalized intensity of sample MP-t5 is obviously enhanced by more than 4.1 times that of the as-deposited sample, and it is even about 1.6 times stronger than the normalized PL intensity of Ge-V contained diamond with a particle size of 650 nm made in our previous HFCVD

experiments.^[17] Furthermore, this result is in agreement with that of microwave plasma-treated Si-V center contained diamond crystals,^[26] suggesting that the termination state of the particle surface changes from hydrogen termination state to oxygen termination state.

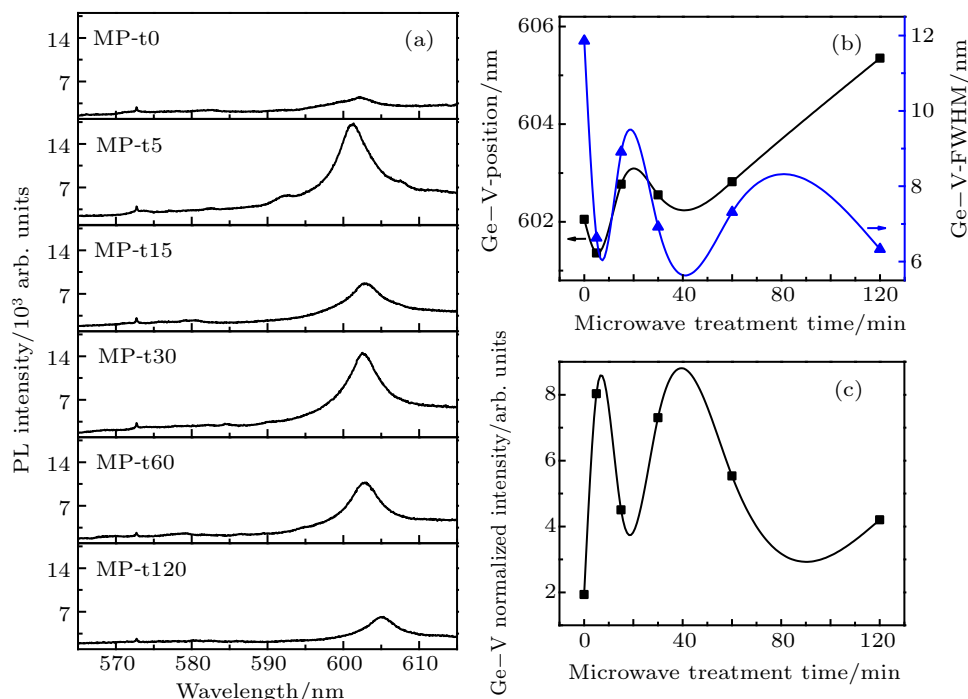


Fig. 2. (a) PL spectra, variation of (b) position and FWHM values and (c) normalized intensity of Ge-V PL peak of samples with microwave oxygen plasma treatment time.

With treatment time increasing to 15 min, the Ge-V PL intensity of sample MP-t15 becomes weaker than that of sample MP-t5. After that, the PL intensity of MP-t30 is enhanced again. Then, the Ge-V PL intensity of sample MP-t60 becomes weak. Within 60 min of treatment, the normalized intensity of Ge-V PL increases and decreases alternately, and the position of Ge-V peak fluctuates around 602 nm. We find that the Ge-V PL intensity of sample MP-t5 is the strongest and the FWHM is narrower, indicating that the short-term microwave oxygen plasma treatment has the greatest improvement in the Ge-V PL properties of diamond particles. However, after 120-min microwave oxygen plasma treatment, the Ge-V PL intensity weakens and the position of Ge-V peak shifts to the right, near 605 nm. This suggests that after long microwave oxygen plasma treatment, the lattice stress around the Ge-V centers changes greatly, and the Ge-V center structure is slightly damaged. Within 120 min of microwave oxygen plasma treatment, the Ge-V PL intensity of diamond changes continuously, but it is always stronger than that of the as-deposited sample, confirming that the microwave oxygen plasma treatment can significantly improve the Ge-V PL intensity. In addition, combining the above results of FESEM and PL tests, we find that the Ge-V PL intensity of sample with smooth surface is stronger than that of sample with rough surface.

To understand the change of Ge-V PL properties of diamond particles with microwave oxygen plasma treatment time increasing, we measure their Raman spectra, which are shown in Fig. 3. In Raman spectra, the characteristic peak near 1332 cm⁻¹ relates to diamond.^[27] The peak between 1550 cm⁻¹ and 1580 cm⁻¹ is called G peak, which indicates the existence of graphite.^[28] The peak at 1350 cm⁻¹, called D peak, relates to the disordered carbon. The peaks at 1140 cm⁻¹ and 1470 cm⁻¹ are peaks of trans-polyacetylene (TPA), which relate to the hydrogen (H) atoms.^[29] Figure 3(b) displays the plot of position and FWHM value of the diamond peak *versus* microwave treatment time. The content of diamond phase, graphite and disordered carbon are calculated according to the formula in Ref. [30] and the results are shown in Fig. 3(c).

After 5-min microwave oxygen plasma treatment, the diamond peak position of sample MP-t5 is closer to 1332 cm⁻¹ than that of the as-deposited sample, and the FWHM value reduces to 6.2 cm⁻¹, revealing that the diamond quality is significantly improved. As the diamond phase increases from 80.84% to 93.94%, the graphite content decreases from 1.50% to 0.35%, and the disordered carbon content decreases from 5.81% to 1.76%. Combining with FESEM analysis, it is speculated that microwave oxygen plasma treatment has etched graphite and disordered carbon on the particle surface, mak-

ing the internal regular diamond crystal exposed. The exposure of internal crystalline diamond is considered to be related to the Ge-V PL enhancement of sample MP-t5. Moreover, the TPA content decreases significantly, which indicates that the H atoms in the particles significantly decrease.

However, the diamond peak of sample MP-t15 becomes wider, the content of diamond decreases while the graphite and disordered carbon increase. Considering the rough surface shown in Fig. 1(c), we suspect that some of the exposed diamond has been converted into graphite and disordered carbon. Due to the conversion described above, the number of Ge-V centers in the particles slightly decreases, which leads the PL intensity of MP-t15 to decrease. With the increase of microwave oxygen plasma treatment time, the FWHM of the diamond peak of sample MP-t30 decreases again, diamond content increases while graphite and disordered carbon de-

crease. Therefore, the reason why the Ge-V PL intensity of the sample MP-t30 is enhanced is that the graphite and disordered carbon on the particle surface are etched by the oxygen plasma. Then, the diamond quality and content of the sample MP-t60 decrease again.

Raman spectra show that the phase composition of the particles changes alternately. It is presumed that the phase composition near the surface of the particles consists of the graphite and disordered carbon at the beginning, and then the diamond, graphite and disordered carbon occur alternately. The results show that the short-term microwave oxygen plasma treatment is benefit to removing the graphite and disordered carbon from the surface of the particles, but if the time is extended, part of diamonds will inevitably be converted into graphite and disordered carbon.

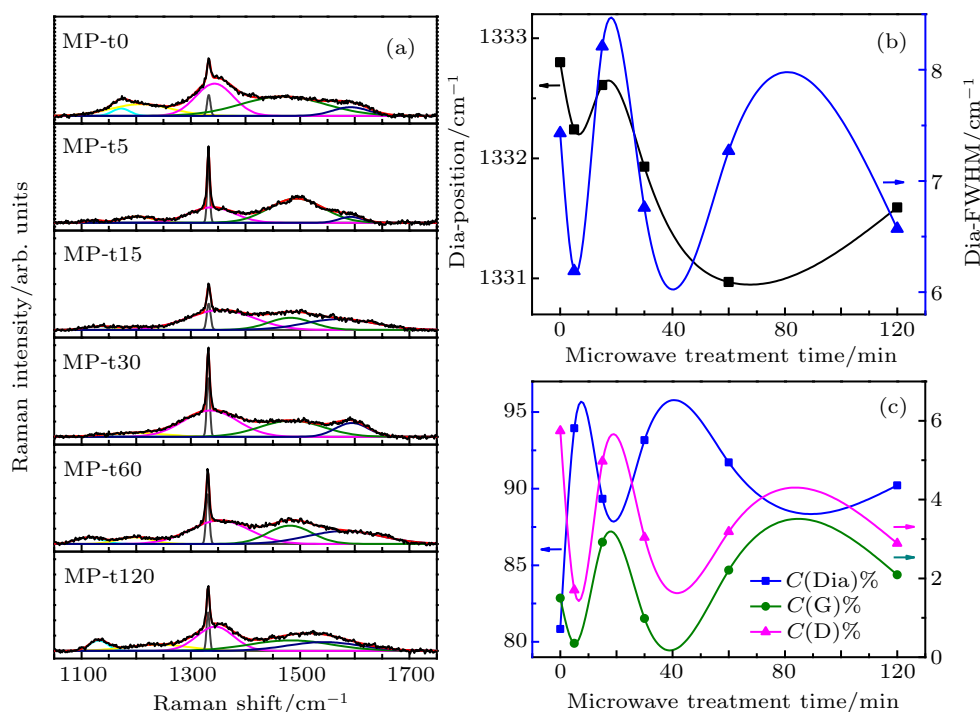


Fig. 3. (a) Raman spectra, (b) variation of position and FWHM of diamond peak in Raman spectra with microwave oxygen plasma treatment time, and (c) variation of diamond, graphite, and disordered carbon content of samples with microwave oxygen plasma treatment time.

We believe that there are two reasons for the alternate changes in Ge-V PL intensity. One is that the number of Ge-V centers decreases gradually due to the conversion of some diamond into graphite and disordered carbon. Figures 3(b) and 3(c) indicate that the change trends of graphite and disordered carbon content are opposite to that of diamond content, and they are the same as variation trend of FWHM values of diamond peak. It shows that the reduction of non-diamond phase is conducive to the improvement of diamond content and quality. Combining Fig. 2(c) and Fig. 3(c), the variation trend of graphite and disordered carbon content are the same as that of diamond Ge-V PL intensity. This suggests that both graphite and disordered carbon (D peak) greatly weaken the Ge-V PL

intensity. As is well known, the G peak is the main factor that quenches the PL intensity of color center in diamond.^[22,31,32] However, we find that the disordered carbon also plays a key role in quenching the PL. The other reason is the change in H atom content in the particles, which is shown by the change in TPA content. The content of TPA decreases greatly at first, but it changes slightly later. Also, the Ge-V PL intensity is enhanced to the strongest value at first, indicating that the reduction of H content at the beginning of the treatment enhances the Ge-V PL intensity.

Combining the above results of FESEM, PL and Raman tests, we reveal the relationship between Ge-V PL properties and the microstructure of diamond particles as shown in Fig. 4.

In the initial stage of microwave oxygen plasma treatment, the content of H is significantly reduced, while graphite and disordered carbon are etched, exposing diamond crystals to the surface of particles, resulting in a significant increase of Ge-V PL intensity. Next, the cycle of ‘diamond is transformed into graphite and disordered carbon, then graphite and disordered carbon are etched’ occurs. These cycles are accompanied by changing the particle surface morphology and Ge-V PL intensity. The presence of less non-diamond phase makes the particle surface smoother, which corresponds to a stronger Ge-V PL intensity (darker blue). For samples containing more graphite and amorphous carbon atoms, the reduction in diamond quality and content will result in weaker Ge-V PL intensity (lighter blue). In addition, the roughening of the particle surface scatters the emitted light and can affect the intensity of Raman and PL intensity. In these cycles, the particles are continuously etched and the size is reduced. After several cycles, the particles gradually become irregularly spherical, and the number of Ge-V centers in the diamond decreases.

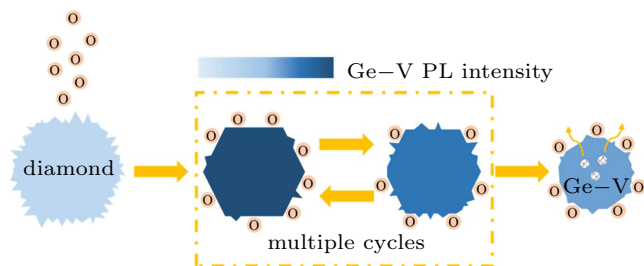


Fig. 4. Schematic illustration of relationship between Ge-V PL and microstructure of diamond particles.

4. Conclusions and perspectives

In this work, we investigate the effects of microwave oxygen plasma treatment on the structure and PL intensity of dispersed Ge-V diamond particles. The experiments show that microwave oxygen plasma treatment etches the graphite and disordered carbon on the surface of the particles at the beginning, and subsequently there is the cycle of ‘diamond is converted into graphite and disordered carbon, then the graphite and disordered carbon are etched’. When some diamond is converted into graphite and disordered carbon, the particle surface becomes rough and the Ge-V PL intensity decreases. Then the graphite and disordered carbon phase are etched, the smooth surface appears and Ge-V PL intensity increases again. It is indicated that not only graphite but also disordered carbon weakens the Ge-V PL intensity. The Ge-V normalized intensity is greatly improved after 5-min treatment, which is about 4 times stronger than the Ge-V normalized intensity of the as-deposited sample. Then, the Ge-V PL intensity increases and decreases alternately during microwave oxygen plasma treatment, but it is always stronger than the Ge-V PL intensity of the as-deposited sample. The results suggest that the short-term microwave oxygen plasma treatment has the greatest optimization effect of diamond quality and Ge-V PL properties. Our study provides a feasible way of enhancing the Ge-V PL

properties and effectively controlling the surface morphologies of diamond particles.

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