Adhesion's Macroscopic Exhibition of CVD Diamond Films on Si Substrate and Its Relationship with Film's Microstructure

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Abstract

The adhesion force of a CVD diamond film on a Si substrate was detected by direct tensile tests. The test was performed on a tensile testing rig equipped in a S570 scanning electronic microscopy, and the whole testing process (load-strain curve) was recorded. By means of Raman spectrum analysis and SEM photography, the relationship between the microstructure of the diamond film and the macro-exhibition of the adhesion force is found and a reasonable explanation of this phenomenon is given.

Introduction

The technology of diamond film synthesis by chemical vapor deposition (CVD) develops rapidly and is becoming more and more popular since Eversole's first success in vapor deposition of diamond on diamond seeds in 1953 [1] and Matsumoto *et al.*'s great advances in CVD diamond using various activation techniques [2-4]. Due to their excellent properties, possible application fields of diamond films are widespread. Adhesion strength should be one of the most important properties when diamond films are used as a cutting tool, a heat sink, an optical window or a protective layer in integrated circuits etc.

For the deposited film, the adhesion failure implies that a separation occurs at a sharp interface between the film and the substrate on the microscopic scale. The force which causes the adhesion failure is defined as the adhesion force [5]. Due to its practical importance, the quality of the adhesion of thin films has received considerable attention and a number of methods have been devised to characterize the adhesion. Common methods include the scratch test, the indentation test and the peel test [6-7]. Besides these, some special methods such as the lap shear test [8], the substrate bending test [9], centrifugal method [10] and the acoustic microscope image method [11] are used for special applications. All these methods can and only can determine the critical force when the deposited film is separated from the substrate, that is, adhesion force.

The adhesion of a diamond thin film on a Si substrate can also be determined by any methods mentioned above. When its adhesion is known, one tries to study the factors that effect the adhesion and then to improve them to meet the practical requirement. A lot of work has been down on this field, but there is still little work on the effect of the microstructures on adhesion between a thin diamond film and the Si substrate.

In the present work, we use a SEM equipped with a tensile testing rig to study the thin diamond film's adhesion. The main test is direct tensile test. It differs from the ordinary test that not only the final adhesion force, but also the whole test process, can be recorded through both the *in situ* SEM observations and the real time strain-stress measure. From all the recorded information, we can know both the macro-exhibition of the interfacial adhesion and the corresponding microstructures of the diamond film and Si substrate during the loading process, and find some relations between these two phenomena.

Experiment

Sample preparation

The crystalline silicon (100) was used as the substrates. Samples of four groups with dimension of $11 \times 15 \times 0.5 mm^3$ were used in the experiment. Each group has three samples. Different pretreatment were done on the four groups, and then diamond was deposited via an electron assisted chemical vapor deposition set using different CH_4 concentration for every group.

After deposition, all sample groups got a diamond film 20 μm in thickness. The quality of the films was characterized by a Raman spectroscopy. The film's microstructures were also investigated by a scanning electron microscopy.

Adhesion measurements

The adhesion measurement system is shown sketchily in Fig. 1. To perform the tensile test, two steel bars, with one end having the same area as the sample, were made. Samples were glued to steel bars with epoxy resins. The bars were pulled along the direction indicated

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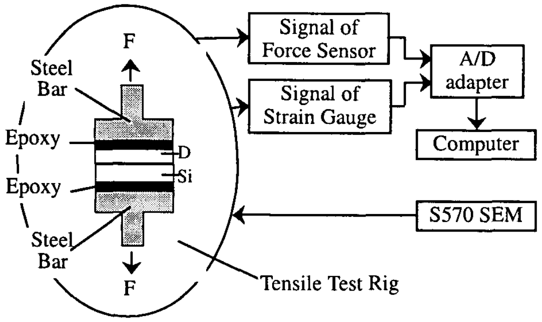

Figure 1: Illustration of peel test system.

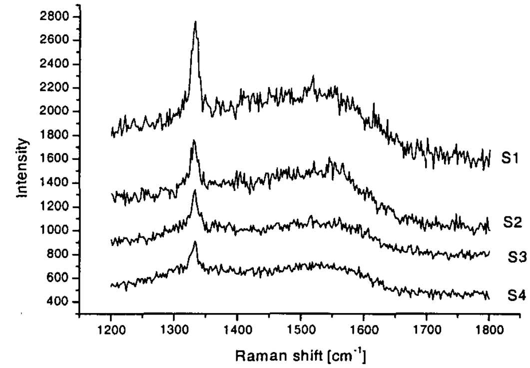

Figure 2: Raman spectrum of diamond films. The letter refers to the sample groups.

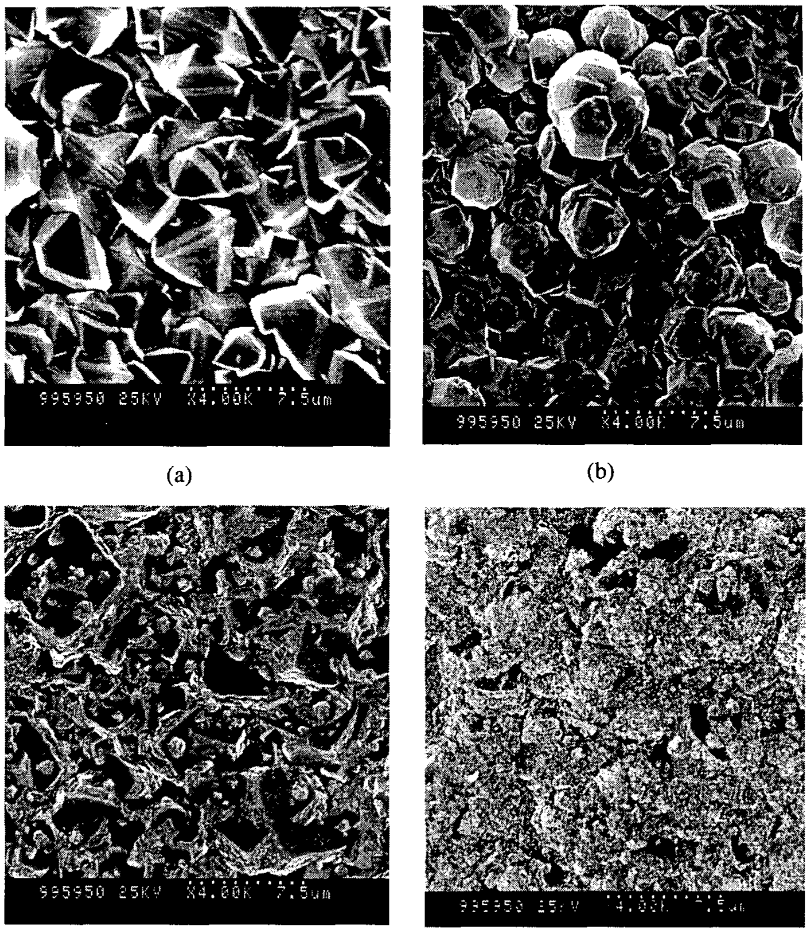

Figure 3: SEM picture for diamond thin films
(a) S1 ; (b) S2 ; (c) S3 ; (d) S4

in Fig.1 by the tensile testing rig equipped in the S570 scanning electron microscopy. The whole process was performed under SEM observation.

Results and Discussion

Microstructures of diamond films

The Raman spectrums of the diamond films are shown in Fig. 2. All the spectrums have a sharp diamond peak at 1332-1334cm^{-1} and a weak, broad peak of amorphous carbon at 1550cm^{-1} nearby. The difference in the peak heights (intensities) is caused by different CH_4 concentration.

Nemanich has presented an approximate formula of the peak width w and the grain size L: [12]

$$wL \approx 70\left(cm^{-1}\right)\left(nm\right). \qquad (1)$$

We can use Eq. (1) to determine the grain sizes of the four sample groups. The results are listed in Table 1. It is seen that the grain sizes of groups S1 and S2 are relatively big, while those of S3 and S4 are relatively small. This corresponds to the SEM pictures, which are shown in Fig. 3. In S1 and S2, the films present remarkable crystals. The crystals in S1 are tetrahedrons with (111) facets. Twins and voids were found in the picture. The crystals in S2 are octahedrons with (100) and (110) facets. Voids were also found in it. The difference in the grain size between S1 and S2 is not distinct as we can see in the picture. On the contrary, the crystals in S3 and S4 are not obvious and the films seem continuous. It is supposed that there are a lot of tiny agglomerated grains. The grains in S4 are more compact than those in S3 which has some grapes that make the film like spumescence.

Table 1: Grain sizes of the four samples

	S1	S2	S3	S4
w (cm^{-1})	14	16	20	18
L (nm)	5.0	4.4	3.5	3.8

Measurement of the adhesion force

The adhesion forces of the samples were measured by the tensile testing rig. Force sensor and calliper were used in the rig to measure the load and strain. Bonds failing by other modes, e.g., Si fracture, failure at other interfaces or load failure, were eliminated from the experiment. The final data were obtained by eliminating the effect of steel bars' strain changes. The error of the testing system is below 3%. Considering some uncertain factors such as the thickness of the epoxy, the error of the results is estimated not bigger than 5%. However, due to the difference of the sample quality, the scatter of the measured load-strain curves in each group is a little bit larger. The measured load-strain curves of four samples, which are the best ones chosen from the four groups respectively, are shown in Fig. 4. The adhesion forces calculated from the curves are listed in Table 2.

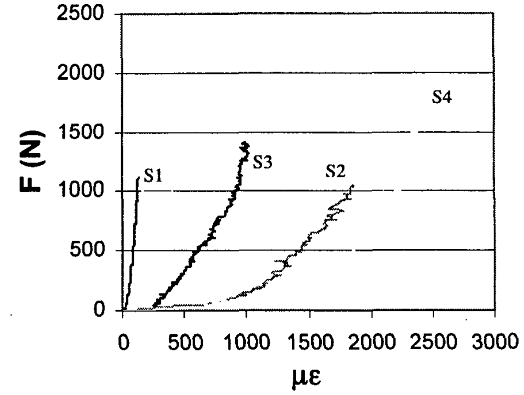

Figure 4: Load-strain curves of four samples.

The curves of the four samples record the whole loading process of the test. They have the same trend, and all of them include three different stages. At the initial stage, strain increases rapidly with load. This is mainly due to the deformation of the epoxy resin. The second stage corresponds to the possible deformation at the interface of the diamond film and the substrate. During this stage the load increases further but the strain increases very slow. In the final stage, load raises cause little strain changes. The interface has no extra deformation with the increasing load. The relation of the diamond film and the substrate resist the load nervously. This status lasts until the film separates from the substrate thoroughly, and the load at this final point is reasonable to be taken as the adhesion force. It can be seen from Table 2 that the adhesion forces of the four specimens are in the order of S2, S1, S3 and S4 from small to big.

Table 2: The adhesion forces of the four samples

	S1	S2	S3	S4
Adhesion force (MPa)	6.67	4.84	8.48	11.52

The relationship between the microstructure and the adhesion force

From the microstructure observations of the diamond films, it is obvious that the grain size is a dominant factor of the adhesion force. S1 and S2 have bigger grain size, and their adhesion force is smaller. On the contrary, S3 and S4 have smaller grain size, and their adhesion force is bigger. The main reason of the difference might be the contact area between the film and the substrate. With the film embedded in the shape of a wedge at the fine grain boundaries due to the relatively fine grains on the interface, the contact area of S3 and S4 are larger than that of S1 and S2.

Based on this point of view, it is easy to explain the further difference between S1 and S2, or S3 and S4. Though both S3 and S4 have continuum films, the film of S3 has some grapes and is looser than S4. So the contact area of the interface is less than that of S4. This results in the smaller adhesion than S4. Most grains in S1 are tetrahedrons. The interface of two grains relies on the edge and the face of the tetrahedron, and that makes relatively more contact area. The grains in S2 are octahedrons, which are close to sphericity. As well known, the contact area between two spheres or a sphere and a plane can only be a point, so the adhesion of S2 should be lower than that of S1.

Conclusions

The adhesion force of the CVD diamond film on Si substrate was investigated by direct tensile test performed on the tensile testing rig equipped in the S570 scanning electron microscopy. The Raman spectrums, the microstructures' SEM observations, the load-strain curves of the tensile test and the final adhesion forces of the diamond film are presented. From the investigation of the results, we found there should be certain relation between microstructure and the macro-exhibition of the diamond film. If the size of diamond grains is large, the adhesion force should be low; whereas, the adhesion force should be high. Besides these, the grain shape, the twin and the void cavities in the film also are important factors to the adhesion force, due to the contact area of the interface between diamond film and the Si substrate.

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