Jpn. J. Appl. Phys. Vol. 31 (1992) pp. L 1305–L 1308
Part 2, No. 9A, 1 September 1992

Application of the Focused-Ion-Beam Technique for Preparing the Cross-Sectional Sample of Chemical Vapor Deposition Diamond Thin Film for High-Resolution Transmission Electron Microscope Observation

Masayoshi TARUTANI, Yoshizo TAKAI and Ryuichi SHIMIZU

Department of Applied Physics, Faculty of Engineering,
Osaka University, 2-1 Yamada-oka, Suita-shi, Osaka 565

(Received April 2, 1992; accepted for publication June 30, 1992)

Atomic-scale observation of chemical vapor deposition (CVD)-diamond/silicon interface structures was successfully performed by applying a focused-ion-beam (FIB) technique for preparing the cross-sectional samples. Several severe conditions such as weak adhesion and extreme difference in sputtering yield have virtually prevented the proper processing of the interface cross sections by only the conventional method. A sample preparation procedure is proposed with some specific devices for extreme thinning, sufficient for high-resolution transmission electron microscope (HRTEM) observation, emphasizing the good potential for wider practical use.

KEYWORDS: focused ion beam, CVD diamond, cross-sectional sample, HRTEM, interface structure, β-SiC

§1. Introduction

In crystallographic studies of current complex materials, it is important, in fact, necessary, to observe their cross-sectional structures with atomic-scale resolution via high-resolution transmission electron microscopy (HRTEM). Such studies, for example on the interface structures between evaporated thin film and substrate, have been commonly performed with the conventional sample preparation method[1] using lapping, dimpling and ion milling. Many attractive experiments such as the observation of GaAs–$Al_xGa_{1-x}As$ multilayers[2] have been reported so far. However, most of the previous cross-sectioning studies have been laborious, and detailed efforts and, furthermore, the applicable materials have been limited to those with plural composition of similar properties for ion etching.

In the case of the chemical vapor deposition (CVD)-diamond/silicon interface, which is one of the most extreme cases, severe conditions such as weak adhesion and extreme difference in both hardness and sputtering yield between diamond and silicon have hindered the preparation of the cross-sectional samples, except for a few lucky samples.[3] Despite our best efforts, interface breakage at each process or selective overetching of the silicon substrate under ion milling have always spoiled the sample. Hence, we have deemed the focused-ion-beam (FIB) technique as necessary, and are now able to apply it to the cross-sectional sample preparation.

Recently, the FIB technique has become a powerful tool for semiconductor device fabrication of a submicron scale. Ohnishi *et al.*[4] and Ishitani *et al.*[5] have reported many applications of the FIB such as maskless etching, micromachining and device transplantation. Some LSI research and development laboratories have routinely been extending this technique to prepare cross-sectional samples for scanning electron microscope (SEM) observations.[6]

In the present paper, a procedure of the cross-sectional sample preparation technique is presented, with several specific devices using the FIB process, which leads to extremely thin slicing. HRTEM images of CVD-diamond/silicon interface structures are shown, which support the good potential of this method in this case, as well as its application for wider practical use.

§2. Sample Preparation

Diamond thin film was grown on a Si (111) wafer as thick as about 4 μm by plasma-enhanced chemical vapor deposition (CVD). By crushing the wafer, triangular fragments with (111) cleaved surfaces were made. One of the fragments of less than 1 mm^2 with a sharp wedge was chosen as a sample for FIB processing. The fragment was mounted using epoxy glue and Ag paste on a special copper plate for FIB processing and TEM observation under a binocular microscope. Great care was taken in order to adjust both the sample height with the normal objective plane of the electron microscope, and the observable direction with ⟨110⟩, as shown in Fig. 1.

FIB processing was performed as follows. The specimen was first lightly coated with gold to prevent the sample from charging up during the FIB processing. Second, tungsten film was also deposited on it by decomposing $W(CO)_6$ (i.e., FIB-induced deposition[7]) of as much as 4 μm in thickness at the sharp wedge area of the specimen under FIB irradiation. It should be noted that this thick tungsten layer plays a particularly important role in keeping the processed plane smooth. Then, FIB processing was performed in three steps from outside to inside, as shown in Fig. 2(a). If the FIB were to be scanned otherwise, i.e., from inside to outside (reverse direction of that indicated in Fig. 2(a)), then thick redeposition layers would delay the processing, and considerable contamination would be left behind on the sliced surfaces. This quite often does not allow for HRTEM observation. This redeposition problem has

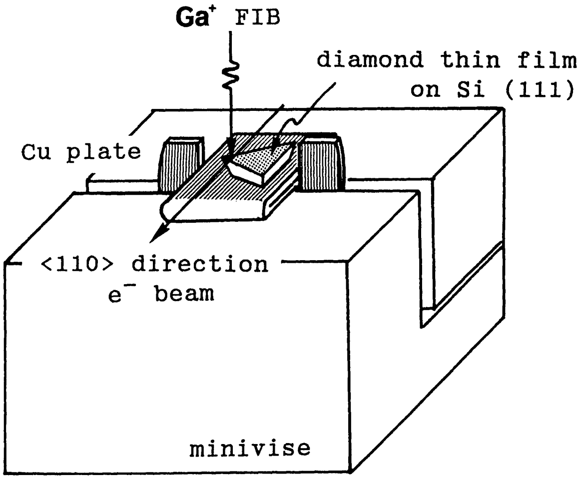

Fig. 1. Schematic of apparatus for sample preparation. The directions of both FIB processing and TEM observation are depicted by arrows.

already been discussed in the beginning stage of the development of the FIB microfabrication technique by Yamaguchi *et al.*[8] The wedge corner was further tapered into a shape akin to a knife edge, as shown in Fig. 2(b), where some vertical columnar profiles appeared on the processed Si surface, as indicated by arrows, reflecting the roughness of the diamond film. If the FIB was unstable or had no tungsten protective film, this roughness would be worsened and would spoil the sample. This is because once the FIB suffers the reflection effect caused by the worsened roughness, the recovering processes cannot restore the smoothness of the sliced surface. Upon approaching the finishing, the specimen current was weakened using a smaller aperture to make the sliced surfaces smoother. At the end, the FIB was scanned diagonally in order to obtain a quite thin area for HRTEM observation. Finally, cross sections 10 μm long and less than 0.3 μm thick were obtained. The entire process was performed very precisely, with the superb aid of a scanning ion microscope (SIM) image. In the present experiment, the ion source was gallium, the accelerating voltage of the ion beam was 30 kV and the total beam current was about 1.5 μA. It took 4 hours to prepare one sample.

§3. TEM Observation

For comparison, both a simply cleaved sample and a FIB-processed sample were observed with JEM-200CX and JEM-4000EX electron microscopes, by setting the samples in a holder, as shown in Fig. 3. Figures 4(a) and 4(b) show TEM images of the two samples. Both maintained their interface adherence, which has never been accomplished, in our experience, by grinding or polishing in combination with ion milling. The cleaved sample had a sharp wedge but the observable area was narrow. On the other hand, the FIB-processed sample had a quite wide observable area of as large as 40 μm^2. The tungsten film was sputtered out entirely, as can be seen in Fig. 4(b), and no dislocations caused by FIB irradiation were recognized. The damaged depth may well be presumed to be tens of nanometers judging from the uncrystallized contrast at the side wall where the FIB was scanned

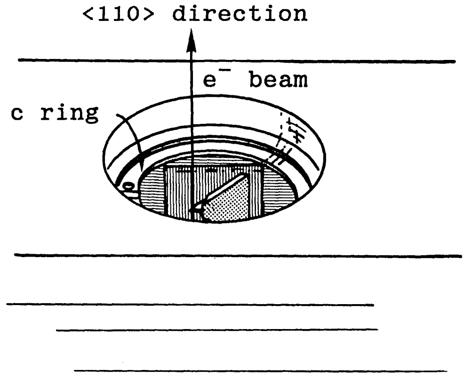

Fig. 3. Schematic of a TEM gonioholder with the FIB-processed sample.

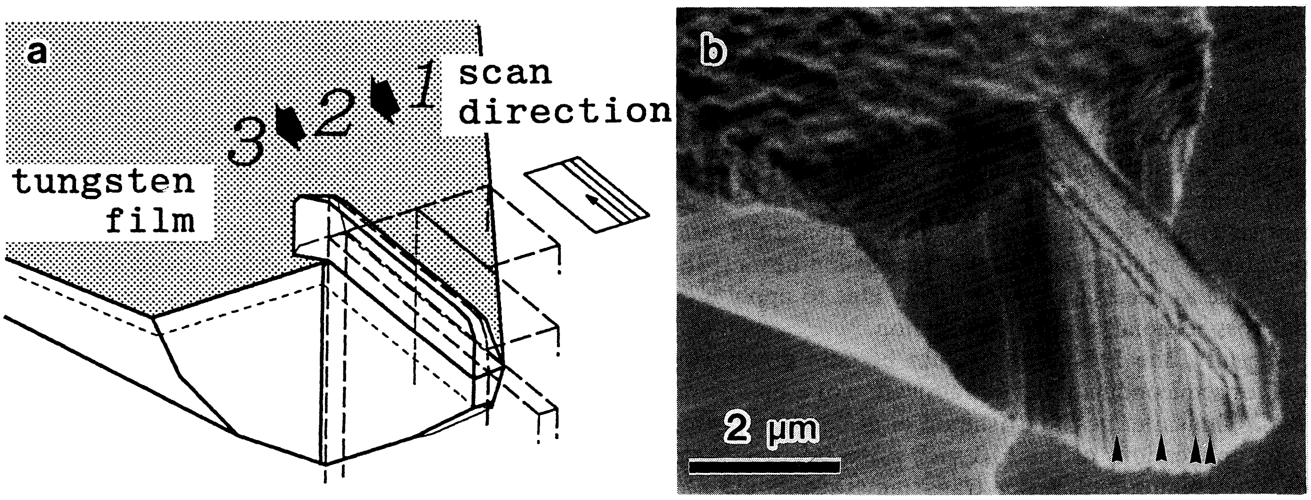

Fig. 2. FIB processing. (a) Schematic of FIB processing. The process must be performed from outside to inside in order to prevent harmful redeposition. (b) SIM image of the FIB-processed sample under FIB processing. Vertical stripes can be seen corresponding to the irregular shape of the diamond layer. Its roughness diminished and the sliced surface became smooth when the FIB was weakened.

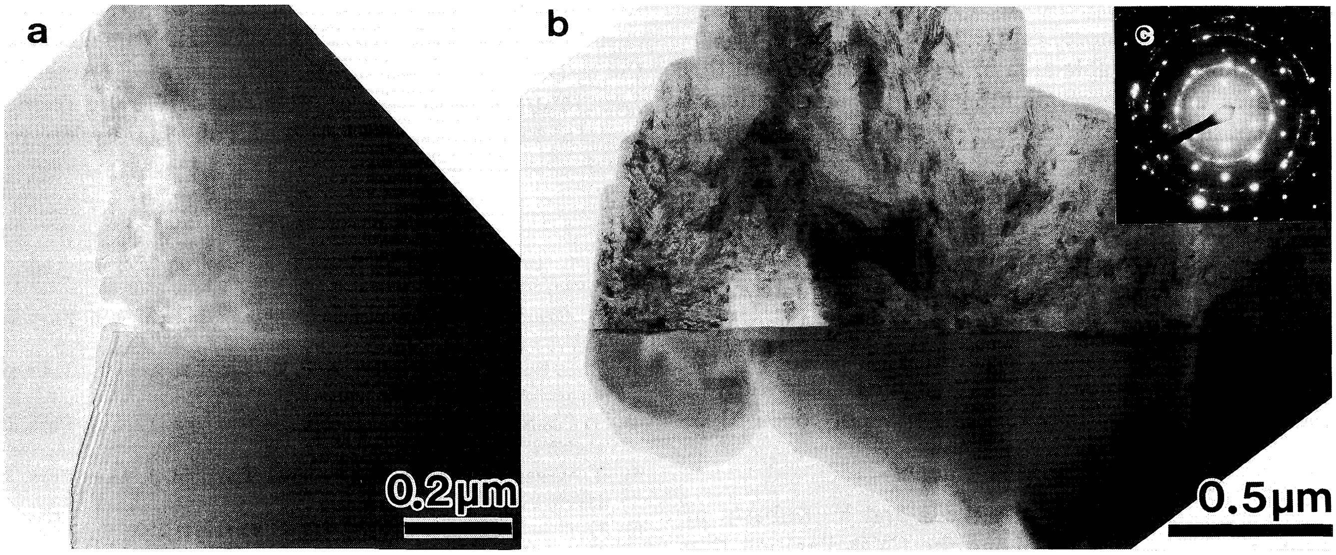

Fig. 4. Cross-sectional TEM images of CVD-diamond thin film (JEM-200CX). (a) Simply cleaved sample. (b) FIB-processed sample. (c) Transmission electron diffraction image of the FIB-processed sample.

diagonally. It can also be seen from the diffraction pattern in Fig. 4(c) that the contamination was very slight.

Figures 5(a) and 5(b) show HRTEM images of the two samples. β-SiC particles were observed within the intermediate regions between the diamond and the silicon substrate in Figs. 5(a) and 5(b). Three spacings of the Si(111) plane, β-SiC (111) plane and diamond (111) plane were resolved in Fig. 5(b). We have inferred from these observational results and some other experiments that the interface was constructed of a thin amorphous intermediate layer less than 4 nm thick which contained scattered zinc sulfide-type SiC (β-SiC) particles. The intermediate precipitates grew epitaxially to the substrate with diameters of from two to several nanometers. The layer proved to be the weakest part mechanically and determined the adhesive strength of the film. The image contrast of the cleaved sample was superior to that of the FIB-processed sample, mainly because the FIB-processed sample was thicker. The contamination on the processed surfaces caused by the FIB reduced the image contrast to some extent; however, the degradation of the image quality was not so severe. Thus, FIB processing enabled cross-sectional observation within a wider area and with atomic- or lattice-scale resolution.

§4. Conclusions

The cross-sectional sample preparation of the diamond/silicon interface by the conventional method has been known to be quite difficult, because the interface is very fragile due to the severe conditions as described. For this reason, the present sample preparation method with FIB has proven to be very useful, accommodating HRTEM observation, and it can advance the systematic study of crystal growth due to its ease and reli-

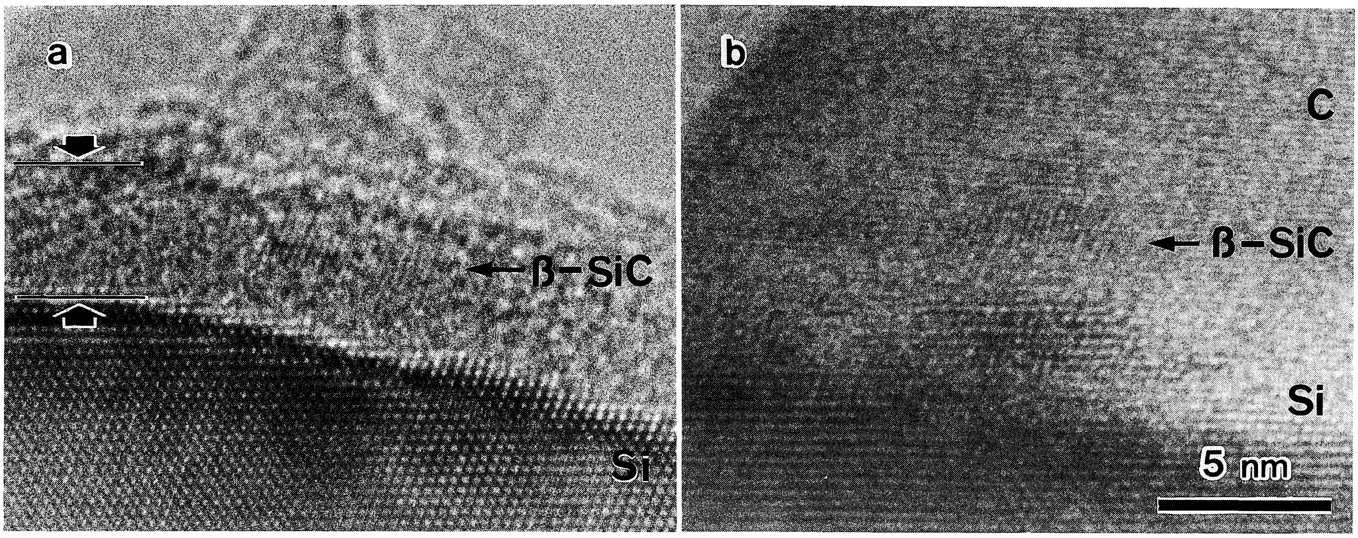

Fig. 5. HRTEM images of the interface structures between diamond thin film and silicon substrate. (a) Cleaved sample (JEM-200CX). An amorphous intermediate layer can be seen at the area indicated by arrows. (b) FIB-processed sample (JEM-4000EX).

ability. (The same experiment has recently been reported in ref. 9.) Furthermore, this technique allows us to obtain a wider observable area of a given sample, and this wide area under observation enables the more intimate nature of the structures to be revealed. It is also an advantage that the FIB can process the samples accurately at a precise position in a desired direction with the aid of an SIM image. The cross-sectional sample thus prepared, however, is not free from contamination due to redeposition, resulting in the degradation of image quality, and from the damage caused by FIB processing. A more detailed investigation of this problem is to be undertaken. An approach to this end using a crystallographic study of the diamond/silicon interface will be reported shortly.

Acknowledgements

We wish to thank Drs. T. Ikeda and K. Kobashi of Kobe Steel, Ltd. for supplying the CVD-diamond thin film. We would like to acknowledge the kind support and advice on processing the sample using the FIB of Mr. T. Matsumoto and Dr. H. Koyama of the Mitsubishi LSI Research & Development Laboratory. Technical assistance for the finishing processing with the fine focused Ga^+ ion beam provided by Dr. H. Yamaguchi of the Hitachi Production Engineering Research Laboratory is gratefully acknowledged. We are further grateful to Professor Y. Ishida of Tokyo University for invaluable discussions.

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