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1999 J. Phys.: Condens. Matter 11 L191

(http://iopscience.iop.org/0953-8984/11/20/101)

J. Phys.: Condens. Matter **11** (1999) L191–L197. Printed in the UK PII: S0953-8984(99)03390-1

LETTER TO THE EDITOR

Observation of defects in a C_3N_4/diamond/Si structure by infrared light scattering tomography

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Received 13 April 1999

Abstract. A structure of C_3N_4 and diamond multilayers on Si(100) substrate was prepared by plasma enhanced chemical vapour deposition and magnetron sputtering techniques. Morphology observation and chemical composition analysis of the structure were performed by scanning electron microscopy and energy dispersive x-ray analysis. The multilayers of C_3N_4 and diamond on Si substrate were clearly observed and the composition ratio of nitrogen to carbon was close to 1.33. Defects in this structure were, for the first time, investigated by infrared light scattering tomography. Most defects in C_3N_4 and diamond multilayers were introduced by an extended growth of the original defects in Si substrate determined through layer-by-layer tomography. The defect type is analytically discussed.

1. Introduction

The synthesis of C_3N_4 film based on the theoretical works of Cohen [1] and Liu [2] was successfully realized using various physical and chemical vapour deposition methods. Cohen proposed from his theoretical calculation that a C_3N_4 compound would be a new super-hard material of a covalent bonded carbon–nitrogen and would have mechanical properties similar to diamond. He further predicted that the crystal structure of this new compound would be tetragonal. Since this original work, many theoretical and experimental studies have been made during recent years [3–5]. The main motivation for these studies was to experimentally justify the theoretical prediction for a new material that may not exist in nature. Several groups reported synthesizing C–N films on different substrates in their laboratories [6, 7]. Recently, a group in the Institute of Physics in China published a series of research works on synthesizing the prototypes of C_3N_4, α-C_3N_4 and β-C_3N_4, which include those predicted by Cohen, as well as some unidentified C–N phases [8–12]. Their results of x-ray diffraction and transmission electron microscopy indicated that the C_3N_4 film was composed of a single crystal. Earlier works directly synthesized carbon nitride film on a Si substrate, but the lattice parameters of C_3N_4 on Si were about 10% larger than those theoretically predicted. A diamond film was therefore prepared between a C_3N_4 film and a Si substrate.

Despite the many studies on synthesizing C_3N_4 film, no report on defects has appeared. However, defects may be an important factor affecting the practical application of this structure in the future. We therefore synthesized C_3N_4/diamond multilayers on a Si(100) substrate to investigate the defects in this structure.

2. Experiment

Si wafers taken from a single crystal of p-type Si(100) used as the substrate were polished and cleaned. One of them was installed in an experimental chamber of an electron cyclotron resonance chemical deposition apparatus, to deposit a diamond layer of nearly 3 μm by the plasma enhanced chemical vapour deposition (PE-CVD) method using CH_4/H_2 mixing gas. The temperature of the specimen was maintained at 650 °C by a temperature controller and the total gas pressure was carefully kept at 3.9 kPa through two flow meters during the five hour deposition process. Thereafter, carbon nitride film was deposited on the diamond layer covered on Si substrate by reactive radio frequency magnetron sputtering technique using a mixing gas of pure graphite (99.9%) and nitrogen (99.999%). The base pressure in the vacuum chamber was under 3×10^{-3} Pa and the working pressure was kept unchanged during the two hour deposition process. Thus a C_3N_4 film nearly 3 μm thick was obtained.

Defects in this structure were detected by 90° infrared light scattering tomography (IR-LST-90°). An optical arrangement of IR-LST-90° is shown in figure 1, where a beam from a YAG laser ($\lambda = 1.06\mu$ m) is finely focused to about 6–8 μm in diameter by a condenser lens and then impinged into the specimen along [001] direction. When the laser beam is scanned on an internal (100) plane of the specimen along [010] direction, the light scattered by the defects in the specimen is continuously accumulated into the TV camera. The data of light scattered in the camera is stored in the frame memory and reconstructed by a computer system to obtain ideal tomography images. A detailed review of this process has been published [13].

Layer-by-layer tomography of IR-LST-90° was used to determine the three-dimensional construction of defects in the structure and the detecting procedure is simply described as follows. A laser beam scans at an internal plane in the specimen to take the tomography image there. The laser beam is then returned to its original position and moved down an interval along the thickness direction of the specimen to take another tomographic image on a new internal plane. By repeating this process many times, we obtain a set of tomographic images, taken from different planes along the thickness direction of the specimen. All the images are

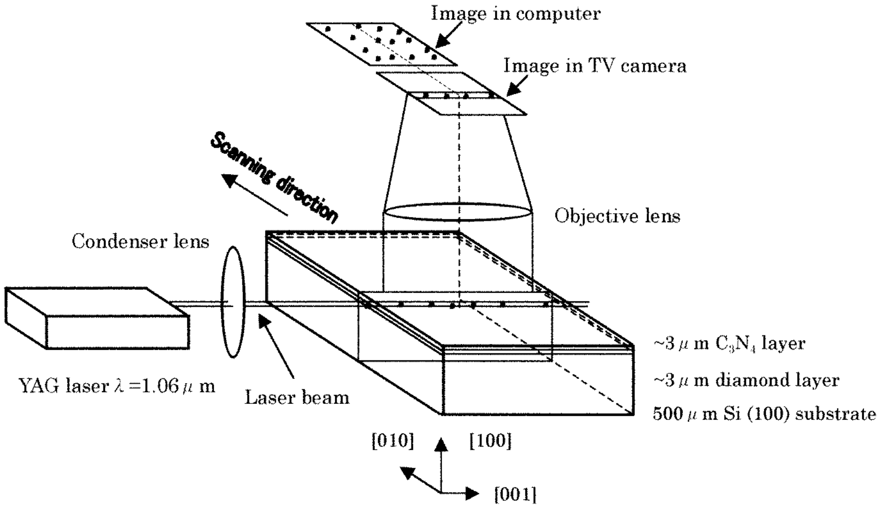


Figure 1. Optical arrangement of infrared light scattering tomography.

proportionally piled up, thus the three-dimensional shape of defects in the specimen is clearly visible.

Morphological observation and chemical composition analysis of the structure were carried out using a JEOL JSM-5200 and a Hitachi S-4200 scanning electron microscope (SEM), in which an Oxford-6566 instrument was installed.

3. Results and discussion

The structure was cleaved at a (001) plane to observe its cross-view morphology by SEM. The result is shown in figure 2, where three parts corresponding to the C_3N_4/diamond multilayers and Si substrate are clearly visible. The energy dispersive x-ray analysis (EDXA) image of the structure is shown in figure 3, in which C, N and Si elements are uniformly distributed in C_3N_4/diamond layers and Si substrate. The composition ratio of nitrogen to carbon in the C_3N_4 layer is close to 1.33.

Defects in the structure were systematically observed by IR-LST-90°. Since we were mainly interested in the interactive relationship of defects between the different sublayers and the Si substrate, the layer-by-layer tomographic images were taken continuously from the C_3N_4 surface through to the 200 μm internal plane in Si substrate. Four characteristic tomographic

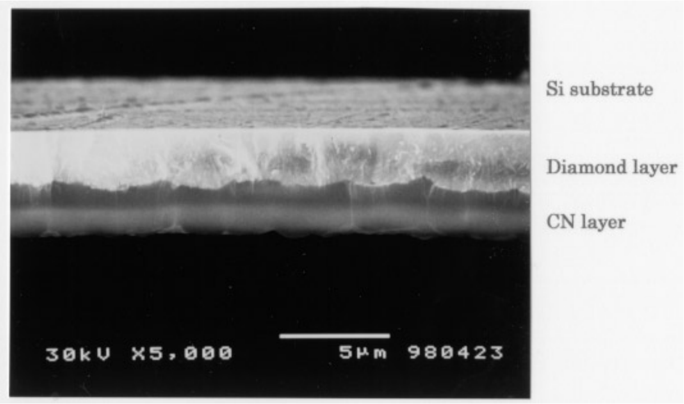
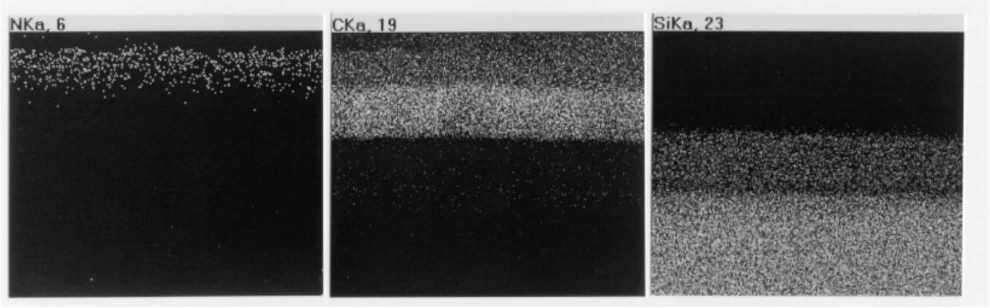


Figure 2. Cross-view morphology of the C_3N_4/diamond/Si structure.



(a) (b) (c)

Figure 3. Chemical composition of the C_3N_4/diamond/Si structure: (a) nitrogen distribution; (b) carbon distribution; (c) silicon distribution.

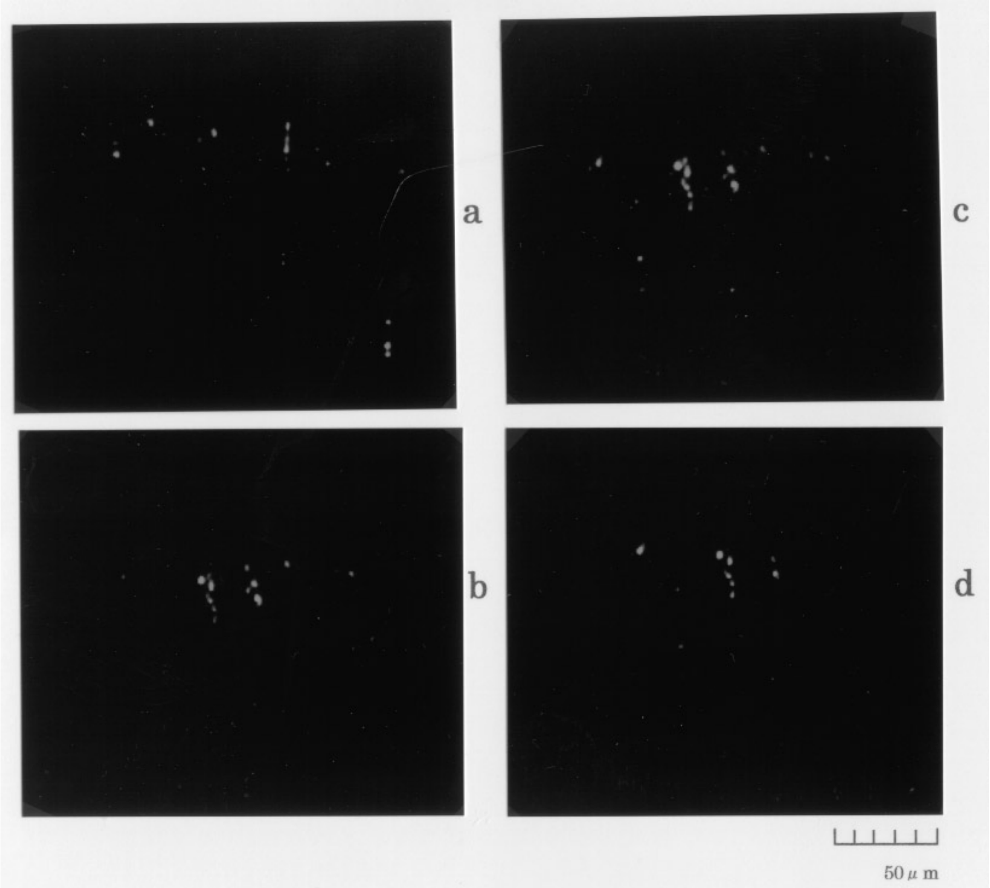


Figure 4. Tomographic images of the defects in the C_3N_4/diamond/Si structure. (a) Silicon substrate (10 μm under structure surface). (b) Silicon substrate (8 μm under structure surface). (c) Diamond layer (4 μm under structure surface). (d) C_3N_4 layer (2 μm under structure surface).

images are chosen to analyse the interactive relation of the defects in different layers and the Si substrate as shown in figure 4. The images in figure 4(a) and (b) were taken from the 10 μm and 8 μm planes in the Si substrate, while the tomographic images (c) and (d) were obtained from the 4 μm and 2 μm planes in the diamond and C_3N_4 layers, respectively. For all these images, white spots of a few micrometres in size due to the defects in the structure are clearly seen. Careful observation of the defects in these images shows clearly that most of those in C_3N_4/diamond multilayers were closely related with the original defects in Si substrate.

To conveniently analyse the defects in figures 4(a)–(d), corresponding drawings are provided, figures 5(a)–(d), where A, B and C represent the regions of the defects which coexisted in both the C_3N_4/diamond sublayers and the Si substrate, respectively. Region A involved a few defect spots existing in (a), (b) and (c) images, meaning that the original defects located at the 10 μm plane in the Si substrate extended into the diamond layers. Region B simultaneously appears in the four images (a), (b), (c) and (d), where the number of defects changes corresponding to different layers in the structure. This indicates a process: original defects extend from the Si substrate to the C_3N_4/diamond layers and two of them disappear

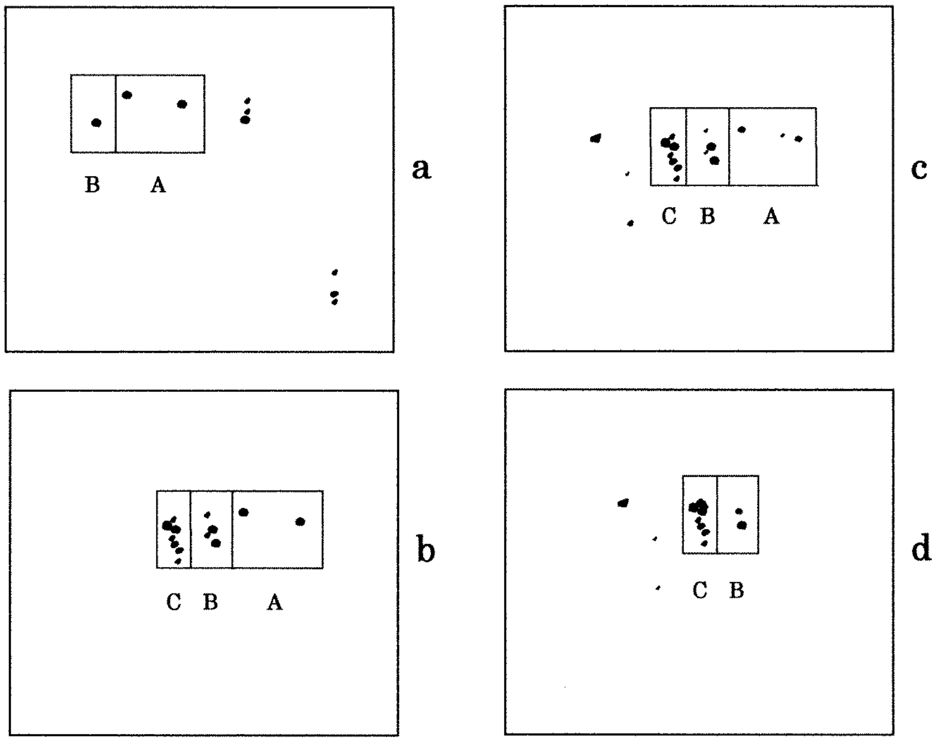


Figure 5. Schematic drawing of defect extended tracks.

in the C_3N_4 layer. Furthermore, a group including more than five defect spots is distinctly seen in the C region in images (b), (c) and (d). A noteworthy fact is that the light scattered intensity of original defects in the Si substrate becomes strong when the defects extend to the C_3N_4 and/or diamond layers. From the above results, we believe that most defects in C_3N_4/diamond multilayers were introduced by extended growth of the original defects in the Si substrate. Some independent defect spots positioned in the C_3N_4/diamond layers and the Si substrate in figure 4 were also observed. A tomographic image taken on the 200 μm plane in the Si substrate is shown in figure 6, where one big and several small white spots due to defects are visible. The density distribution of the defects along the thickness direction of the structure is plotted in figure 7, which further supports an experimental conclusion that the defects introduced into C_3N_4/diamond multilayers were due to extended growth of original defects in the Si substrate during the deposition process.

Since most defects in C_3N_4/diamond multilayers were from the Si substrate, the defect type of the structure must be related to that in the Si crystal. Studies over a long period on several main defect types, such as vacancy-type, interstitial-type and oxygen precipitates, have been carried out and it is known that the defects in the present structure are not oxygen precipitates because the Si substrate here is an as-grown crystal. Voids are generally formed by the concentration of vacancies, but are smaller than 1 μm in size, according to many reports [14–16], thus the defects are also not voids. However, interstitials are usually agglomerated to form dislocation clusters of line-like shapes which we have observed in CZ–Si crystals grown under an electromagnetic field and the usual conditions of crystal growth, respectively. The

Figure 6. Tomographic image of the defects on the 200 μm plane in the Si substrate.

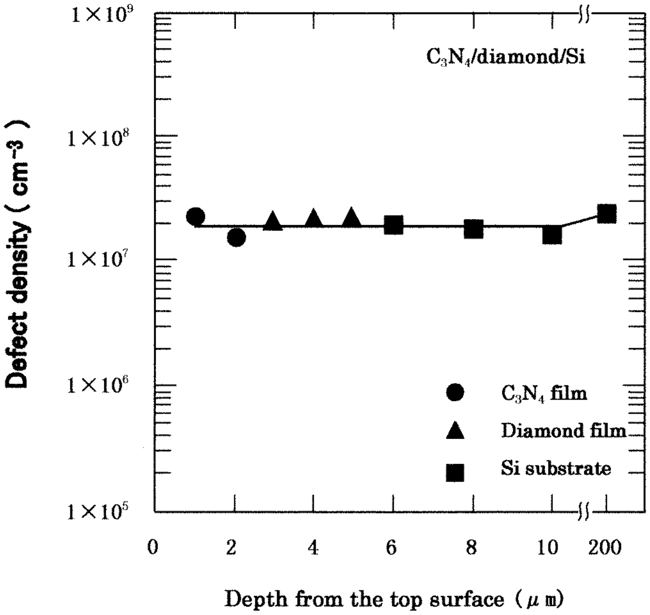


Figure 7. Density distribution of the defects along the thickness direction of structure.

result of layer-by-layer tomography described above makes it clear that the defects here are line-like and nearly 10 μm in length. We therefore believe that the defects in this structure are dislocation clusters agglomerated by an interstitial-type defect.

4. Conclusion

A structure of C_3N_4 and diamond multilayers on Si substrate was synthesized and the defects in this structure were observed. Most defects in C_3N_4/diamond multilayers were introduced by extended growth of original defects in the Si substrate during the deposition process. The density distribution of the defects in the structure further supports this conclusion. The defect type is analytically thought to be dislocation clusters agglomerated by an interstitial-type defect.

This work was supported by JSPS Research for the Future Program in the Area of Atomic Scale Surface and Interface Dynamics under the project ‘Dynamic behaviour of silicon atoms, lattice defects and impurities near silicon melt-crystal interface’.

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