THE SURFACE IMPURITY DISTRIBUTION ON SYNTHETIC DIAMOND

Zhang Shuda
International Center for Materials Physics, Academia Sinica, and
Tianjin Radio & TV University
No.1 Yingshui Road, Nankai district, P.O. Box 220
Tianjin, P.R.China, 300191

The impurity distribution on synthemic diamond surface have been studied in detail. The surface impurities on diamond are determind and analysed by the secondary ion mass spectroscopy (SIMS). Detaileder analyses about impurity depth-profiling have been reported in the paper. Ion erosion method is used. The maximums concentration of the impurities are situated in thin layer near the most outward surface.

INTRODUCTION

Synthetic diamond are used in industry and its physical and chemical properties are paid attention by scientists. Neither natural nor synthetic diamonds are as pure as monocrystalline silicon because diamonds are grown in a condition of high temperature and superhigh pressure. The number of impurity elements in crystalline diamond can be more than 20 and their contents can weigh up to several per cent . The impurity contents, existing forms inside diamond crystal and their effect on the diamond properties have been studied by many authors[1-5]. But impurities at the surface and in the bulk are not the same. Surface impurities (therefore surface properties) have big influence on diamond tools. Studying diamond surface has been accelerated by rapidly developing of surface science. Bogateireva et al[6] studied the effect of impurities on specific resistance. Hydrogen atom acting on diamond surface by Lou Chunping et al[7]. Zhang Shuda and Sun Wei[8] studied the effect of impurities on electroplating.

But what factor concentration and distribution of surface impurities relate to? How is the impurity concentration changes with depth? It is of great significance to study the instantaneous growing process and mechanism of diamond crystals.

ANALYSIS

The following formula can be obtained from SIMS basic principle

$$I_M = C_M \eta R^+ S_M I_O \quad (1)$$

where: I_M----second ion intensity of element M, C_M----concentration of element M on the matrix surface, R^+--ionization rate of element M, S_M--sputtering yield of element M, I_O--primary beam intensity, η----a parameter related to the structure and properties of the instrument.

SIMS in the experiment is not quantitative analysis, but the count rate change of an impurity second ion, according to formula (1), reflects the impurity concentration change in the diamond sample because the matrix (diamond) and measuring conditions are the same.

RESULTS

Different Synthetic Technology

The sample A is made in factory A; the sample B_1 and B_2 are made in factory B but produced with different technology. It is observed that the surface impurity concentrations on the diamond samples sometimes differ very large. For example, $Si(B_1) / Si(A) > 9$, $Ni(B_1) / Ni(B_2) > 9$, Fe(A)

Table 1. Relative Secondary Ion Intensity of The Surface Impurities for Distinct Specific Gravity Diamond.

Nuclear	^{13}C	^{1}H	^{14}N	^{16}O	^{23}Na	^{24}Mg	^{27}Al	^{28}Si	^{39}K	^{40}Ca	^{55}Mn	^{56}Fe	^{58}Ni
Relative intensity (46H / 46L)	1.00	1.83	1.07	2.55	8.67	1.54	2.48	2.33	3.86	2.19	0.67	2.80	2.00

/ $Fe(B_2)$ =5. It is clear that the surface impurity status of the synthetic diamonds are certainly related to their growing conditions. In the following paper, concentrations between two samples differ greatly for the same impurity element because of different growing conditions.

Different Specific Gravity

Since impurity concentrations and their existing forms are not alike in distinct synthetic diamond crystals, these crystal specific gravity are not very much alike. A batch product made by the same technology is separated into two groups by heavy liquid separation method. The specific gravity of sample 46H among them is larger than natural diamond ($3.52g/cm^3$), and another is called 46L. Analysis results of SIMS are shown in table 1.

Different Planes

Big difference has been observed (table 2). Most of the impurity elements, in general, occur more easily on the {111} planes than the {100}. Since the {111} planes surface energy is higher than the {100}, growing velocity of the {111} planes is faster.

Table 2. Impurity Concentrations Compare of the {111} Planes with the {100} Planes.

Nucler	^{13}C	^{14}N	^{27}Al	^{28}Si
Relative impurity concentration {111} / {100}	1.00	16.8	5.25	3.76

Depth-Profiling

In order to obtain the depth-profiling of the surface impurities, the ion erosion method is used. When we study impurity depth-profiling, C_M in formula (1) is a function of primary ion erosion time t, i.e. $C_M(t)$. The current of the primary argon ion with 15 keV is 0.5 μA and it is scanning in 500μm square all the time while the samples are eroded and measured. The determined samples are the synthetic diamond made by the static pressure catalyst method. The sample C is a high quality (perfect crystal form, high compressive strength, less inclusions and bright and lustrous colors) and the sample D is a low-grade. The time totals 6400s and the distance between a group of counts and next is 2 min. The whole 50 group counts are obtained. Every count time is 100ms. N, Na, Mg and Si are chosen for the objects of study. There is some reason for doing it. Diamonds are mainly classified by their N; Si has tremendous influence to manufacture various diamond tools; Na and Mg possesses high sen-sitivity to be determined by SIMS method. The first count starts while Ar^+ erosion has begun less than 1 sec. The results are shown in figure 1. Front 40 counts of Na are charted and front 20 count of the other 3 elements are only charted in the figure so that we can see the concentrations change with erosion time easily.

In comparison to this test, a broken face of the natural diamond crystal is analysed, it shows none of the phenomena in the figure 1. The results are shown in figure 2. Thus we can conclude that the features in figure 1 are the peculiarities of surfaces growing of synthetic dia-

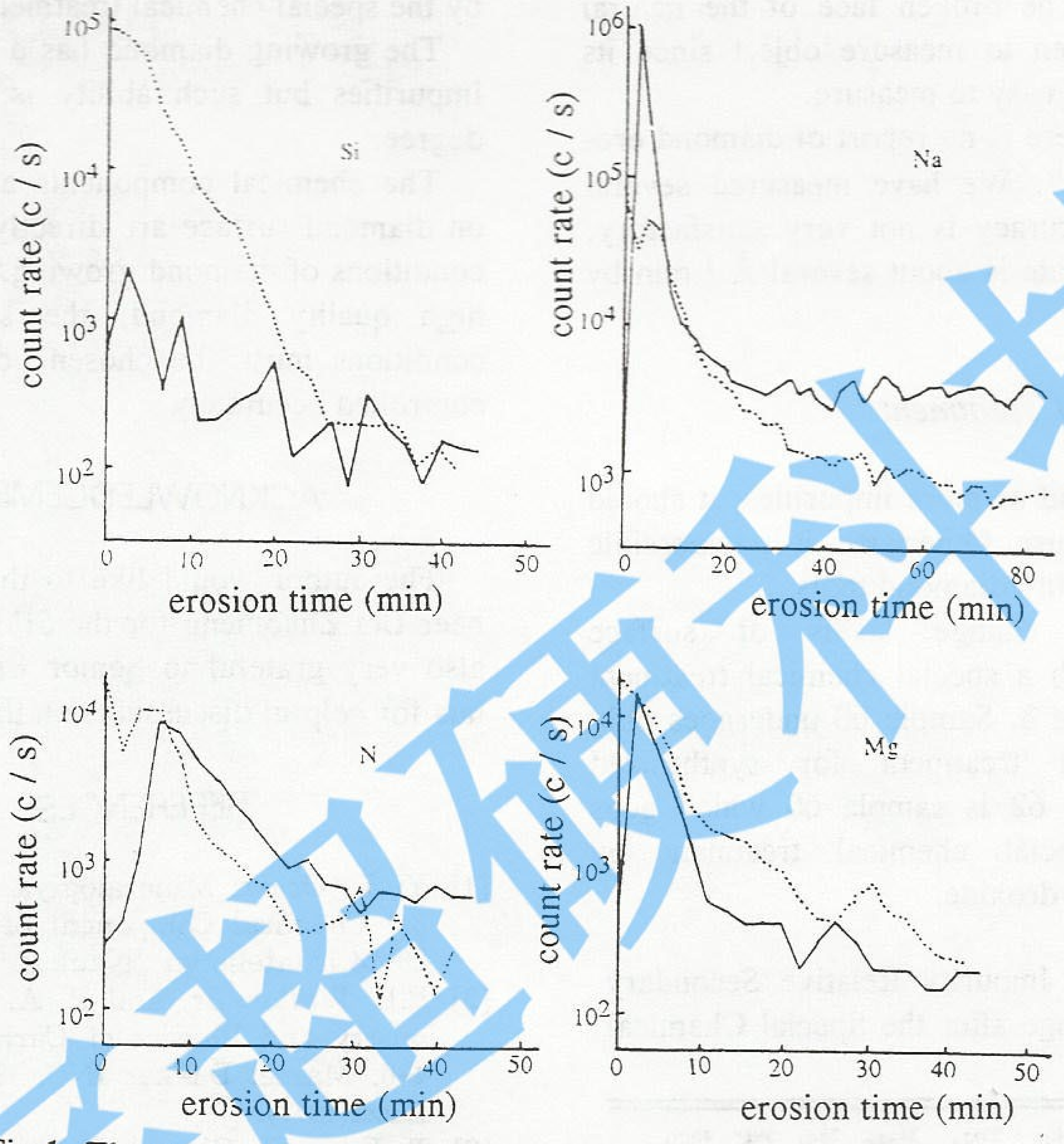

Fig 1. The surface impurity depth-profiling curve on the synthetic diamond.
—— Sample C, ------ Sample D

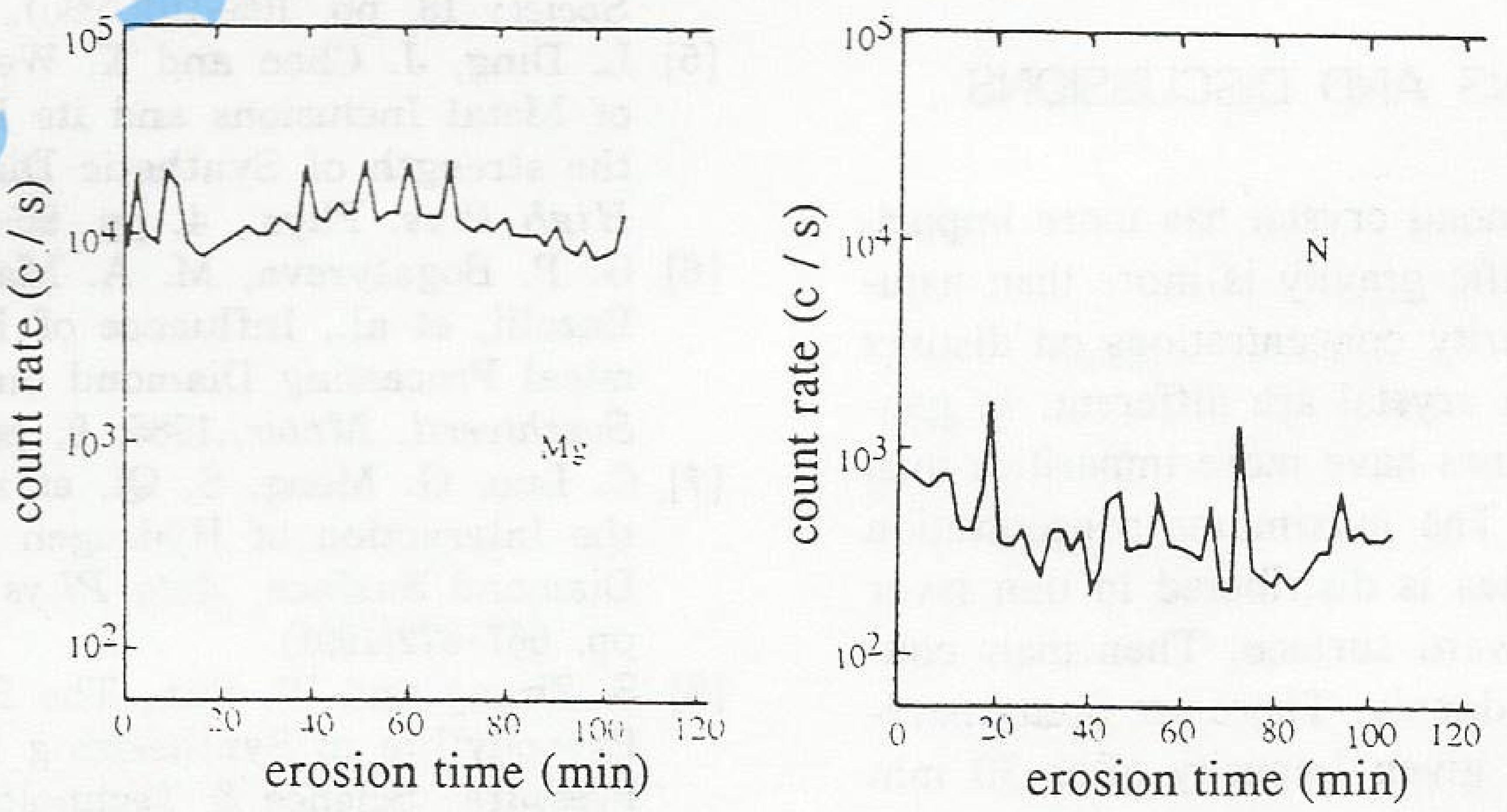

Fig 2. The impurity depth-profiling curve on a broken face of the natural diamond.

mond crystals. The broken face of the natural diamond is chosen to measure object since its size is bigger and easy to measure.

Up to now, there is no report of diamond erosion rate by Ar^+. We have measured several times but the accuracy is not very satisfactory. The determined rate is about several Å / min by 15keV Ar^+.

Special Chemical Treatment

For the diamond of more impurities; it should be treated before use. Otherwise, it is impossible to make good quality diamond tools.

The relative change status of surface impurities through a special chemical treatment are shown in table 3. Sample 60 undergoes only normal chemical treatment for synthesized diamond. Sample 62 is sample 60 which goes through the special chemical treatment by melting sodium hydroxide.

Table 3. Surface Impurity Relative Secondary Ion Intensity Change after the Special Chemical Treatment.

Sample	^{13}C	^{14}N	^{16}O	^{23}Na	^{24}Mg	^{28}Si	^{39}K	^{40}Ca
60	1.00	1.91	0.50	12.29	2.72	6.95	9.17	3.22
62	1.00	1.11	0.30	0.17	2.38	1.25	0.22	0.43

CONCLUSIONS AND DISCUSSIONS

A synthetic diamond crystal has more impurities when its specific gravity is more than natural diamond. Impurity concentrations on distinct planes of the same crystal are different. In general, the {111} planes have more impurities than the {100} planes. The maximums concentration of various impurities is distributed in thin layer near the most outward surface. Then their concentrations drop suddenly. There are pretty nearly the same for a given impurity after 30 min Ar^+ erosion, except there are inclusions. Impurity contents on surface could be reduced greatly by the special chemical treatment.

The growing diamond has a ability to remove impurities but such ability is limited to some degree.

The chemical components and their contents on diamond surface are directly related with the conditions of diamond growing. In order to get a high quality diamond, the suitable synthetic conditions must be chosen carefully and be controlled accurately.

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REFERENCES

[1] Yu.L. Orlov, Mineralogiya almaza, chapter 3, Chemical Component of Diamond, pp. 23-24,Izdatelistvo 《Nauka》,Moscow(1973).
[2] P.L. Walker Jr. and P. A. Thrower, Chemistry and Physics of Carbon, vol. 13, pp. 4-6, Marcel Dekker INC, New York and Basel(1977).
[3] T. Evans,Z. Qi and J. Maguire,The Stages of Nitrogen Aggregation in Diamond, *J. Phys. C: Solid Phys.* 14, L379-384(1981).
[4] S. Zhang, Impurities and Inclusions in Synthetic Diamond, *J. Chinese Ceramic Society* 13, pp. 105-110(1985).
[5] L. Ding, J. Chen and X. Wei, The Change of Metal Inclusions and its Influence on the strength of Synthetic Diamond,*Chi. J. High Pres.* Phys., 4, pp. 96-104(1990).
[6] G. P. Bogatyreva, M. A. Marinich, G. A. Bazalii, et al., Influence of Electrochemical Processing Diamond on its Properties, *Sverhtverd. Mater.*,1985, 6, pp. 13-15.
[7] C. Luo, G. Meng, S. Qi, et al., Studies on the Interaction of Hydrogen Atoms with Diamond Surface, *Acta Phys. Sinica*, 40, pp. 667-672(1991).
[8] S. Zhang and W. Sun, The Functions of Pyrophyllite in Synthesizing Diamond, High Pressure Science & Technology, Abstracts XIth AIRAPT International Conference, part 1, pp. 217-218, Kiev(1987).