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Oxidation kinetics of type 2A natural diamond [100] and [111] surfaces by TG [α]

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Abstract

The recent advances in the synthesis of deposited diamond films have resulted in renewed interest in the kinetics of oxidation of natural diamond on the various crystallographic faces. Data on [111] faces can be obtained only at small percentage conversions because the etched surfaces convert to [100] as the reaction proceeds. Oxidation of [100] faces is initiated at the site of defects and proceeds laterally along the surface rather than into the bulk. Flynn and Wall kinetics may be carried out on [100] faces, but allowances must be made for the fact that the initial density of defects will depend on sample preparation, particularly on the angle between the actual surface and the true [100] direction.

INTRODUCTION

The kinetics of diamond oxidation was first investigated in the early 1960's by Evans and Phaal [1]. Weight loss was determined by dimensional change, and the investigation was limited to extremely small oxygen partial pressure. Nevertheless, the data were remarkably good and some very important results were obtained. It was found that the activation energy on the [100] surfaces differed substantially from that on the [111] and [110] surfaces (approximately 230 and 96–184 kJ mol^{-1} for the [100] and non-[100] surfaces, respectively). Moreover, the mechanism for oxidation seemed to differ substantially on the different crystallographic planes. Oxidation on the [100] planes occurred at step defects, with etching proceeding along the surface rather than down into the bulk. This pattern was not found on the [111] or [110] surfaces, where etching occurred everywhere accompanied by the formation of a carbon layer.

Interest in the oxidation of diamond has been rekindled recently with the discovery of methods for the manufacture of high quality diamond films at technologically useful deposition rates. One of the obvious questions to

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be answered about these new materials is how the properties of deposited diamond compare to those of natural single crystal diamond. Comparisons of a number of properties have been made, including oxidation rates [2]. Unfortunately, such comparisons are extremely difficult and the results must be interpreted with great care. First of all, diamond films are polycrystalline rather than single crystal. The films tend to be textured (i.e. the orientation of the grains is not random). On the other hand, natural diamond cleaves along the [111] plane. Thus, grinding diamond specimens into powder results in a [111] material (commercially available powders are, to the best of our knowledge, not type 2A). Because [111] oxidizes more readily than [100], one may expect the nature of the surface to change, starting with a [111] material but ending with [100]. In order to examine the [100] surface of a natural diamond, large polished pieces must be used, with all the technical problems this implies. In this study, we have examined these problems in some detail. We have found that the difficulties are considerable, but not hopeless.

EXPERIMENTAL

Specimens of natural type 2A diamond were carefully cut and polished to either [100] or [111] surfaces. The [100] pieces were polished on all six sides and were $0.1 \times 0.1 \times 0.025$ cm^3 in dimension. The [111] pieces were polished on the large faces only and were $0.1 \times 0.1 \times 0.01$ cm^3 in dimension.

Specimens were oxidized under pure flowing oxygen (50 cm^3 min^{-1}) in a Du Pont TGA model 951. Some specimens were removed after 10, 20, and 30 percent weight loss and examined using SEM. Others were oxidized completely at heating rates of 0.2, 0.5, 1.0, 2.0, and 4.0 K min^{-1} (nominal). A typical TG sample consisted of three wafers (about 2.5 mg) laid carefully on the bottom of a flat surfaced platinum boat. As discussed below, corrections were made for differences in wafer thickness. Also, because of the small sample masses, instrumental effects were minimized by subtracting an empty pan baseline from each data set. Kinetic parameters were determined by the Flynn and Wall method [3] assuming first order kinetics using Du Pont's TGA Kinetics software.

RESULTS AND DISCUSSION

The effect of oxidation on the [111] surface is illustrated in Fig. 1. The most interesting feature of this oxidized surface is the presence of numerous non-[111] facets, as can be seen by the large number of facets forming right angles with respect to each other. This is to be expected because of the large disparity between the activation energy of oxidation on [111] and [100] surfaces. The effect is identical to that used in etching metallographic

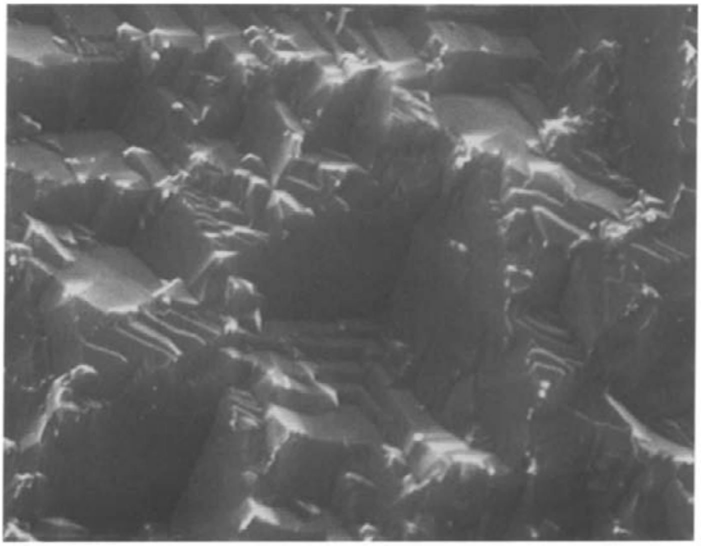

Fig. 1. SEM micrograph of oxidized [111] face following 10% weight loss (original magnification 10000×).

samples for light microscope examination. For this reason, weight loss measurements analyzed by Flynn and Wall kinetic methods are not meaningful. At best, one can try to use powdered samples and do the analysis for relatively small weight losses. We are currently attempting to do this. However, use of wafers does not yield good data.

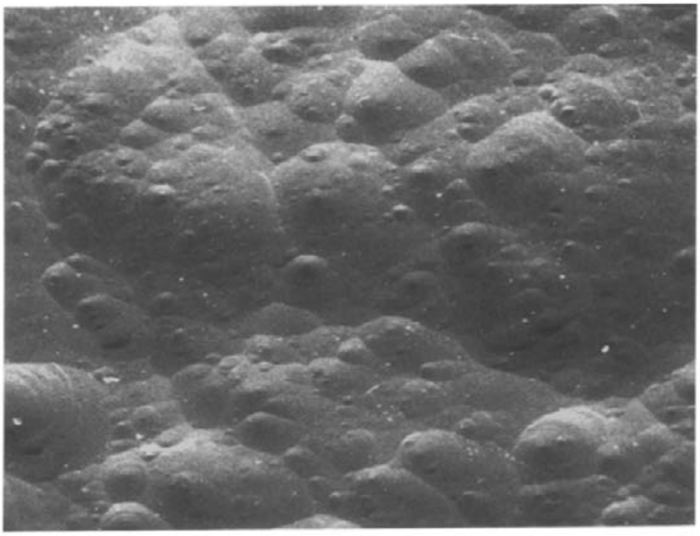

Fig. 2. SEM micrograph of oxidized [100] face following 10% weight loss (original magnification 5000×).

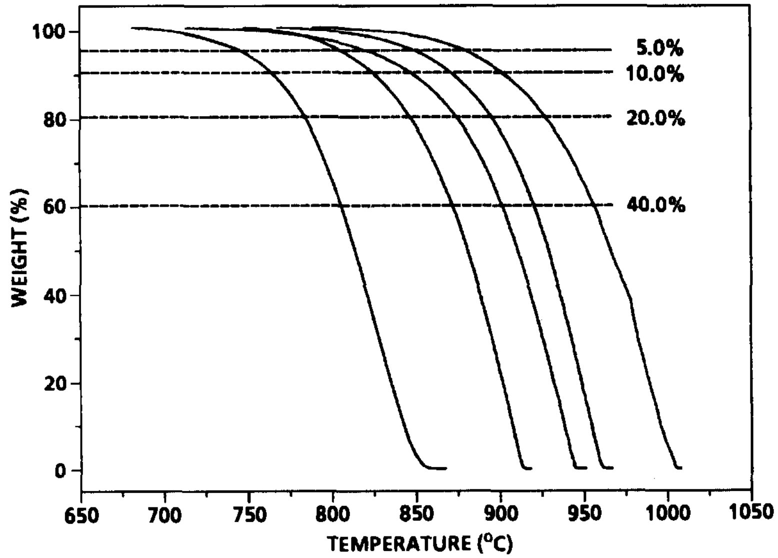

Fig. 3. Sample mass versus temperature of diamond specimens with polished [100] faces at heating rates of 0.18, 0.45, 0.89, 1.81, and 3.64 K min^{-1}.

Oxidation of the [100] surface presents a very different situation [1] as illustrated in Fig. 2. As was observed by Evans and Phaal, oxidation occurs at defects and proceeds laterally across the surface rather than into the bulk. This leads to a pattern of extremely shallow craters, with new craters opening up at the site of newly encountered defects. Tilted stereographic images show that the crater depths are very small (less than a few tenths of a micron). Evans and Phaal observed highly delineated steps on the [100] surfaces oxidized under very low oxygen partial pressure. These steps are not seen in Fig. 2 (pure oxygen), although a few have been found. This indicates that while the primary oxidation mechanism is the same, secondary mechanisms may be present which etch into the surface, thus rounding corners and obliterating the steps.

The sample mass versus temperature is illustrated in Fig. 3 for various heating rates. The actual heating rates were 0.18, 0.45, 0.89, 1.81, and 3.64 K min^{-1}. The curves shown have been corrected for instrumental effects (including buoyancy). Flynn and Wall analysis results are illustrated in Fig. 4. The activation energy is found to be 225–230 kJ mol^{-1}, in excellent agreement with the results of Evans and Phaal. However, the scatter in the data is substantial. Part of the problem is that, unlike powders, where grains become smaller and surface area diminishes, the wafer oxidizes almost entirely from one or two flat surfaces until just before the specimen disappears. This can be seen in the shapes of the curves in Fig. 3 near the bottom (i.e. the sharpness of the bend in the curve at mass equal to zero). Thus, each data set must be cut off at a constant weight loss, or (less easily)

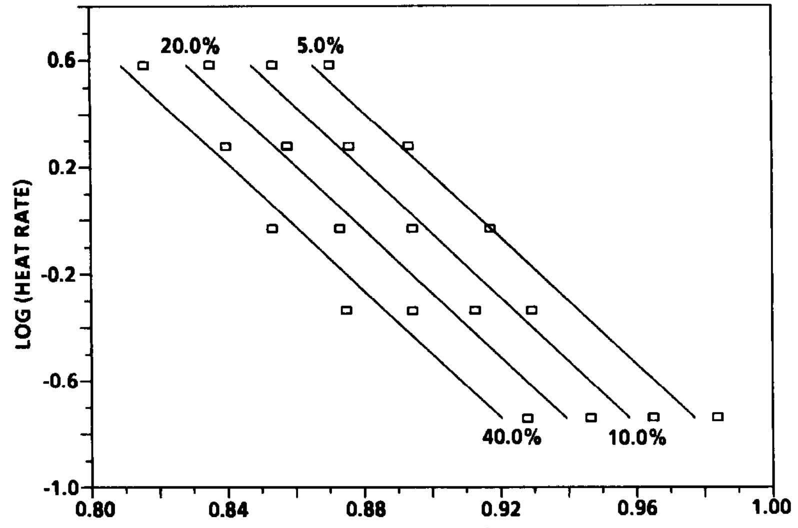

Fig. 4. Arrhenius plot for [100] face diamond wafers in pure oxygen. Data are corrected for instrumental effects but not for variations in wafer thickness.

samples of identical thickness must be used. In the present case, selecting a constant weight loss (1.5 mg) improved the scatter in the data to some degree, as illustrated in Fig. 5. The new activation energy so obtained was 190–207 kJ mol^{-1}. Another problem with the experiment is that the surfaces are not precisely oriented along the [100] direction. They vary over

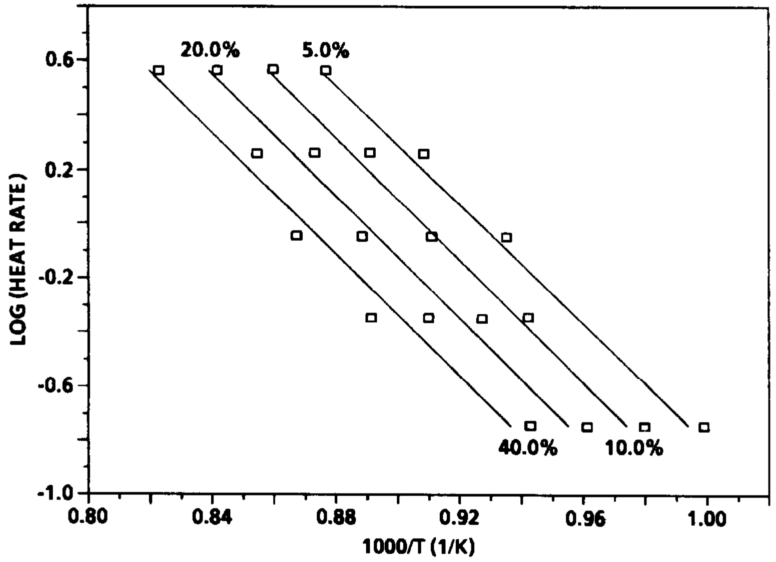

Fig. 5. Arrhenius plot for [100] face diamond wafers in pure oxygen. Data are corrected for both instrumental effects and for variations in wafer thickness.

a range from zero to three degrees. Thus, the initial density of step defects varies from sample to sample. This leads to a highly variable "induction time" resulting in scatter in the data.

The measurements are currently being repeated with several important modifications. Wafers are being matched as closely as possible with respect to the angle between the surface and the true [100] direction. Specimens are being mounted on platinum mesh to assist oxidation of both flat surfaces. Finally, specimens are being pre-oxidized to produce defect densities which are as consistent as possible from one specimen to the next. The results of these measurements will be reported at a later time.

SUMMARY

We have examined the oxidation of natural type 2A diamond in pure oxygen. It was found that meaningful measurement of kinetic parameters was possible only on the [100] face because of the large disparity between the activation energy of oxidation on [100] and non-[100] faces. Measurements made on the [100] faces had to be performed on polished, single crystal wafers. It was found that reasonable data could be obtained provided the data set was truncated after a fixed weight loss. However, considerable scatter in the data was still observed, which we attributed to differences from one sample to the next in the densities of step defects. It was suggested that this scatter could be reduced either by controlling the tilt of the surface from the true [100] direction, or by pre-oxidizing all specimens to induce similar defect densities.

REFERENCES

1 T. Evans and C. Phaal, Proc. 5th Carbon Conf., Vol. 1, Pergamon Press, 1962, p. 147.
2 C.E. Johnson, W.A. Weimer and D.C. Harris, Mater. Res. Bull., 24, (1989) 1127–1134.
3 J.H. Flynn and L.A. Wall, Polymer Lett., (1966) 323.