Co-doping of CVD diamond with boron and sulfur

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Boron is well-established as a p-type dopant in diamond, but attempts to find a viable n-type dopant remain unsuccessful. Recently, sulfur has been reported to give n-type conductivity.[1,2] However, other measurements have indicated that the samples contained boron and were p-type.[3,4] Very recent work has shown that diamond co-doped with sulfur and small quantities of boron shows n-type conductivity, which was established by Mott-Schottky analyses, thermoelectric effect, Hall measurements, scanning tunneling spectroscopy (STS) and UV open-circuit photo-potential.[5-7] At higher boron concentrations, a transition to p-type behavior is observed. Experiments performed without boron in the feed gas showed no sulfur incorporation and no change in conductivity.

For the samples co-doped with boron and sulfur, SIMS analyses show that the sulfur is concentrated in the near surface region. Depth profiles from SIMS showed a decrease of 1-2 orders of magnitude in sulfur concentration from the diamond surface to a depth of 200 nm. The boron concentration remained relatively constant in this range. Similar concentration profiles for sulfur have been observed in all co-doped films surveyed by SIMS regardless of growth time, film quality, and feed conditions. One possible explanation is that excess sulfur is captured at the growth surface and incorporated. As the growth front proceeds, the sulfur diffuses out, possibly aided by vacancy diffusion. Vacancies show a similar depth profile to sulfur.[8]

To investigate the electrical properties as a function of depth, we performed scanning tunneling spectroscopic measurements on a cleaved cross section of a (110) diamond substrate after growth. We obtained I-V traces at regular intervals as the STM tip was moved from the diamond surface to greater depths of the grown diamond film. As shown in the current-voltage-depth profiles of Figure 1, the sample shows n-type rectifying behavior over the entire film depth analyzed. However, there is a sharp decline in the magnitude of the rectifying current below the near-surface region.

There is evidence that the excess sulfur concentrations in the near-surface region are not stable. The excess sulfur is significantly reduced upon treatment at 800°C with a hydrogen plasma. Also, the samples lose much of their conductivity when heated in air. At room temperature and below, the activation energies range from 0.06 to 0.12 eV. Above 400K there is an irreversible loss in conductivity and the activation energy has increased to 1 to 1.5 eV. An example of this behavior for one sample is shown in Figure 2.

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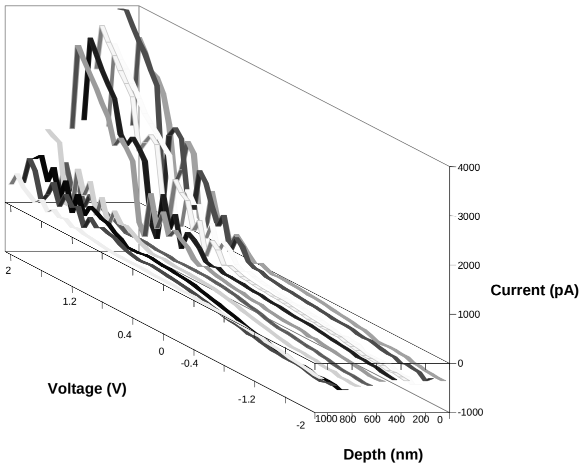

Figure 1. Scanning tunneling current as a function of depth and applied potential for an n-type diamond film on a (110) diamond surface.

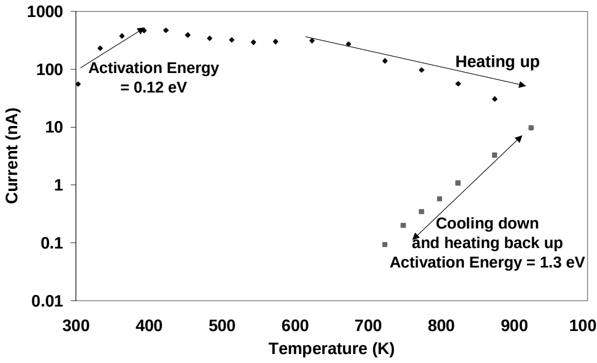

Figure 2. Current versus temperature history for an n-type (111) diamond surface exposed to air.

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