Acceptor level of substitutional Ni in diamond

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Substitutional Ni^- in synthetic diamonds has been investigated by electron-paramagnetic resonance (EPR) and photo-EPR. The photo-EPR investigation shows that the Ni^- EPR signal can be diminished by optical illumination, and the threshold energy of 2.47 ± 0.02 eV suggests that the acceptor level is located at 3.03 eV above the valence band. The energy dependence of the optical cross section for the electron ionization σ_n was determined from an analysis of the EPR transients.

Due to its strong bonding and its small lattice constant it was believed for a long time that transition metal impurities are not incorporated in diamond. This is in strong contrast to all other semiconductors where transition metals were found on substitutional as well as on interstitial lattice sites.[1] Some evidence that transition metals can be present in diamond was found from high pressure synthesis using Ni-Fe solvent and catalysts (leading to the formation of rather large crystals) and Ti-Al getters to prevent high amounts of nitrogen.[2] Such diamonds show distinct luminescence and absorption bands in the visible spectral range which have been tentatively attributed to the presence of Ni in the material.[3] Indeed, in electron-paramagnetic resonance (EPR) studies Ni in diamond was identified.[4,5] It turned out that Ni can be present either in an interstitial or a substitutional lattice position, which seems to depend on the concentration of nitrogen (N) donors present in the sample.

The atomic configuration of neutral Ni is (Ar) $3d^8 4s^2$, on a substitutional lattice position in a group IV semiconductor its neutral configuration is thus $3d^6$. It may act as donor (Ni_S^+, $3d^5$, $S = 5/2$) as well as acceptor (Ni_S^-, $3d^7$, $S = 3/2$), the latter charge state was observed by EPR.[4] It is hence obvious that Ni_S should be an electrically active impurity in diamond. However, the level position and the photoionization cross sections are not known. We will show in this report that Ni_S acts as a deep acceptor in diamond with its $0/-$ level 2.47 eV below the conduction band.

The samples investigated were pieces of about 1/30 Carat cut from a larger diamond synthesized at high pressures and temperatures, unknown amounts of Ni-Fe and Ti-Al were used.

The EPR and photo-EPR experiments were performed on a X-band spectrometer with the sample temperature held constant at 4.2 K during measurement. Illumination of the sample was achieved by a 0.8 mm diameter fiber to which the light of a halogen lamp dispersed by a 0.25 m monochromator was guided. Photo-EPR transients were measured with the magnetic field held at the position of the maximum EPR signal. The photon flux was determined and the optical cross sections were correspondingly normalized. They were obtained by the initial slope technique.[6]

A typical EPR spectrum obtained by cooling down the sample in the dark is shown in Fig. 1. In the central part the signals of substitutional neutral N donors (nuclear spin $I = 1$) are visible.[7] The spectrum was not taken in a high symmetry direction of the crystal, therefore, the outer lines of N are splitted. The central line of N is superimposed on the resonance of the surface dangling bond. At lower magnetic field corresponding to a g value of $g = 2.032 \pm 0.001$ the Ni_S^- signal is detected. The inset shows enlarged the resonance again, the ligand hyperfine (hf) interaction of Ni with the surrounding carbon nuclei are clearly visible. The intensity of these satellite lines and the hf splitting is in agreement with previous investigations,[4] where also the hf interaction with the Ni^{61} isotope (nuclear spin $I = 3/2$, abundance 1.13 %) was resolved. By a comparison with a Si:P standard the concentration of the neutral N donors was determined to be $4 \pm 0.2 \times 10^{16}$ cm^{-3}. For the Ni_S^- we found $5 \pm 1 \times 10^{15}$ cm^{-3}. No other EPR signals were detected, neither in the dark nor under illumination of the sample.

Ni_S^- has a $S = 3/2$ ground state, hence three magnetic resonance transitions should be observable with

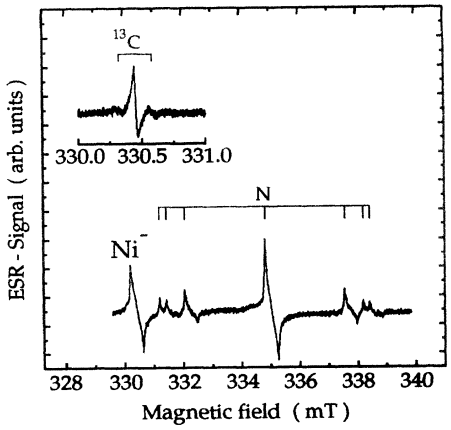

FIG. 1. Electron-paramagnetic resonance signals of Ni_S^- and N^0 in diamond. The inset shows enlarged the ^{13}C ligand hyperfine interactions of Ni_S^-.

the selection rule $\Delta M = \pm 1$, i.e., from $M = -3/2$ to $M = -1/2$, $M = -1/2$ to $1/2$, and from $M = 1/2$ to $3/2$. Random strain present in the sample broadens the $M = -3/2$ to $M = -1/2$ and $M = 1/2$ to $3/2$ transitions beyond detection. Thus, only the $M = -1/2$ to $1/2$ transition can be seen by EPR. It should be anisotropic taking into account the usual spin Hamiltonian description for the $3d^7$ configuration ($S = 3/2$) of a transition metal in tetrahedral symmetry. The anisotropy is very small and buried in the linewidth of the resonance.[4]

The donor level of N (0/+) is known to be located approximately 1.7 eV below the conduction band.[8] The observation of N^0 without illumination of the sample indicates that the Fermi level is located at the $N^{0/+}$ level or even closer to the conduction band. The Ni_S^- signal is also present in the dark, but as already mentioned, decreases by light illumination. The onset is observed at 2.47 ± 0.02 eV (see Fig. 2). Upon monochromatic light illumination the EPR transients showed a monoexponential behavior. This allows to assume that the recharging is a direct process and no other (unknown) levels are involved.

The decrease of the Ni_S^- EPR signal can occur either by electron ionization,

$$Ni_S^- + h\nu \rightarrow Ni_S^0 + e_{cb}, \quad (1)$$

or by hole ionization:

$$Ni_S^- + h\nu \rightarrow Ni_S^{--} + h_{vb}. \quad (2)$$

If process (2) would be the relevant one, the $Ni^{-/--}$ level would be located at 2.47 eV above the valence band. With the Fermi level at or above the nitrogen donor level, Ni should be present in the doubly negative charge state ($3d^8$, $S = 1$), incompatible with the EPR results (see Fig. 3). It is thus the electron ionization we monitor.

From approximately 2.5 eV on the ionization cross section increases, there seems to be a second threshold at energies above 3.1 eV. We attempt to ascribe the energy

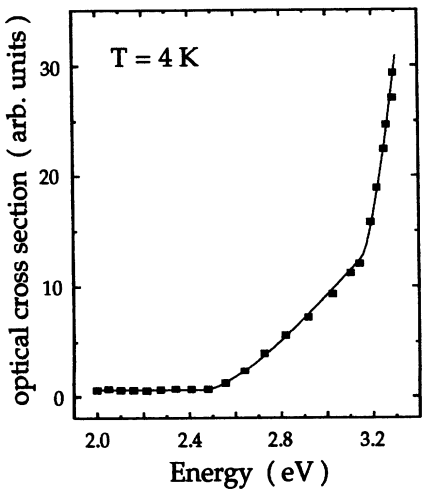

FIG. 2. The energy dependence of the optical cross section for the electron ionization, $Ni_S^- + h\nu \rightarrow Ni_S^0 + e_{cb}$, as determined by photo-EPR.

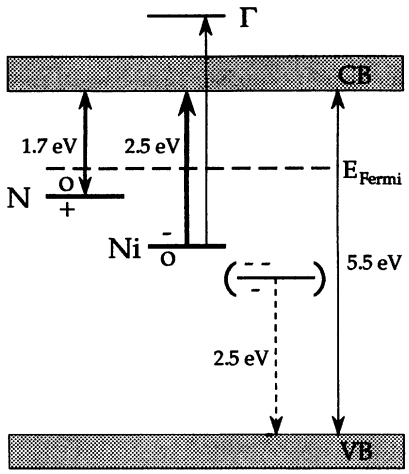

FIG. 3. The energy level diagram of Ni and N in diamond. The observation of a recharging process involving the $Ni^{-/--}$ level (drawn in brackets and dashed arrow) can be excluded from the experiments.

dependence of σ_n within the Ridley model:[9]

$$\sigma_n \sim \frac{(x-1)^{3/2}}{x}; \quad x = h\nu/E_T\ , \quad (3)$$

where E_T is the optical trap depth. A best fit to the curve between 2.4 eV and 3.1 eV (drawn curve in Fig. 2) is obtained for $E_T = 2.47 \pm 0.02$ eV. With respect to the second onset at 3.1 eV it might be related to ionization transitions to the Γ point of the diamond conduction band. It is about 1 eV higher in energy which is in the order one deduces from σ_n.[10]

Diamonds grown with the use of Ni solvents and catalysts are known to show a characteristic green luminescence band with a zero phonon line energy at 2.56 eV.[3] The excitation of this luminescence band requires photons of the energy $h\nu > 3.0$ eV. Thus, it is unlikely that the electron ionization transition of Ni^- is the relevant excitation process. This is in line with the complicated fine structure of this luminescence band which can be hardly described by a recombination involving the $^4A_2$ ground state of Ni_S^-.

Absorption lines at 1.88 eV and 2.51 eV were found in several diamond samples with varying Ni content.[11,12] We observed a strong dependence of the intensity of this absorption lines on the illumination conditions during the measurements. Illuminating the samples prior the absorption measurements with light $h\nu > 2.47$ eV reduces their intensity considerably and may indicate that they originate in Ni_S^-. But indirect recharging processes can also be active. Experiments such as optically detected magnetic resonance which can give a definite assignment are currently under way.

It is interesting to note that diamond is so far the only group IV semiconductor where Ni_S^- is observed in a truly substitutional lattice position with tetrahedral symmetry.[4] In Si and Ge where the lattice bonds are much weaker, Ni_S^- is bond to two neighbor atoms in orthorhombic symmetry.[13,14] Thus, the situation of Ni_S^-

in diamond is more comparable to the $3d^7$ configuration of the transition metals in III-V and II-VI compounds. However, some evidence exists that Ni^+ in diamond can also occupy interstitial positions.[5]

In conclusion, we have determined $Ni^{0/-}$ level position in diamond at 2.47 eV below the conduction band. The energy dependence of the optical cross section for the electron ionization was determined from photo-EPR. Further, work is required before a conclusive description of Ni in diamond is reached, especially there is need for the identification of the internal transitions of this $3d^7$ configuration.

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