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Identification of molybdenum in $6H$-SiC by magnetic resonance techniques

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We report on the identification of molybdenum trace impurities in commercial $6H$-SiC substrates by conventional and optically detected electron spin resonance (ESR, ODESR) and magnetic circular dichroism (MCD) absorption techniques. The two impurity charge states Mo^{4+} $(4d^2)$ and $\mathrm{Mo}^{3+}(4d^3)$ are identified. Consequently, this impurity is electrically active as a deep level acceptor state. In addition we observe the ${}^3A_2 \rightarrow {}^3T_2$ crystal field absorptions of Mo^{4+} $(4d^2)$ in the spectral range 1.1–1.25 eV. The consequences of the present findings, for the use of Mo as an electrical contact material, are pointed out.

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I. INTRODUCTION

Transition-metal impurities in semiconductors are known, and feared, as omnipresent, practically unavoidable contaminations. Their deleterious influence on device performance, in particular on minority carrier lifetime, has been often demonstrated. Within the families of established semiconductors, as silicon and the III-V compounds, an almost encyclopedic knowledge on transition metals now exists. However, for silicon carbide (SiC) such data are still sparse.

For a microscopic identification of transition-metal point defects in semiconductors, magnetic resonance techniques, such as electron spin resonance (ESR) and optically detected electron spin resonance (ODESR), have proven to be most successful. Transition-metal defects identified so far by these methods in SiC polytypes include vanadium and titanium, which are dominant contaminations in as-grown SiC single crystals. For these elements a rather detailed understanding has been elaborated in the past by ESR and ODESR techniques.[1–5] There have also been reports on ESR of manganese[6] and chromium[7] in $6H$-SiC, and on ODESR of scandium[8] in the same SiC polytype. Note that the identification of Cr^{4+} $(3d^2)$ in Ref. 7 is erroneous, the ESR signals actually being due to Mo^{4+} $(4d^2)$, as the resolved hyperfine structure presented in this paper clearly shows.

In this work we want to report on the results of a detailed ESR and ODESR study of *molybdenum* (Mo) impurities in $6H$-SiC. Two charge states of this defect have been detected: Mo^{4+} $(4d^2)$ and Mo^{3+} $(4d^3)$. From these data, the role of molybdenum as a deep-level defect in silicon carbide is suggested.

Two different types of $6H$-SiC samples were investigated in this study. Samples of type (a) were n-type Lely crystals with epitaxial layers grown by the sublimation "sandwich" method[9] and samples of type (b) were n-type and p-type bulk $6H$-SiC wafers, as obtained from CREE Research Inc.[10]

II. ELECTRON SPIN RESONANCE (ESR)

A. Tetravalent molybdenum, Mo^{4+} $(4d^2)$

Spectra were recorded on the Bruker ESP-300 system at 9 GHz. In Fig. 1 we show the ESR spectrum of a type (a) sample, recorded under $H \| c$ and at 20 K. The lines in the center arise from neutral nitrogen donors and from ionized chromium[7] acceptors, Cr^{3+} $(3d^3)$.

The two ESR signals at 0.2254 and 0.4655 T are reported here. Both lines exhibit a sextet structure, as shown in the inset of Fig. 1, resulting from hyperfine interaction of an electron with a central nucleus having nuclear spin $I = 5/2$ and a natural abundance consisting of $(27 \pm 3)\%$ odd isotopes and $(73 \pm 3)\%$ even isotopes, or close to that. The only elements with this property are the $4d$ transition metals molybdenum (Mo) and ruthenium (Ru). Molybdenum has two stable odd isotopes, ${}^{95}\mathrm{Mo}$ (15.9%) and ${}^{97}\mathrm{Mo}$ (9.6%), both having nuclear spin $I = 5/2$. The nuclear moments for these isotopes are very similar, $\mu = -0.910\mu_N$ for ${}^{95}\mathrm{Mo}$ and $\mu = -0.929\mu_N$ for ${}^{97}\mathrm{Mo}$ (μ_N being the nuclear magneton). Since the observed linewidth is about 12 MHz, the overlapping hyperfine sextets cannot be resolved. Ruthenium has also two stable odd isotopes, ${}^{99}\mathrm{Ru}$ (12.8%) and ${}^{101}\mathrm{Ru}$ (17.0%), both having nuclear spin $I = 5/2$. The nuclear mo-

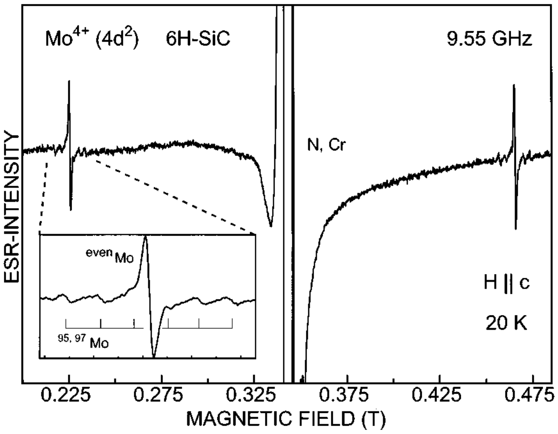

FIG. 1. ESR spectrum of Mo^{4+} $(4d^2)$ in $6H$-SiC recorded under $H \| c$. The ESR signals in the center arise from neutral nitrogen donors and ionized chromium acceptors, Cr^{3+} $(3d^3)$. The inset shows the hyperfine structure due to the odd isotopes ${}^{95}\mathrm{Mo}$ and ${}^{97}\mathrm{Mo}$.

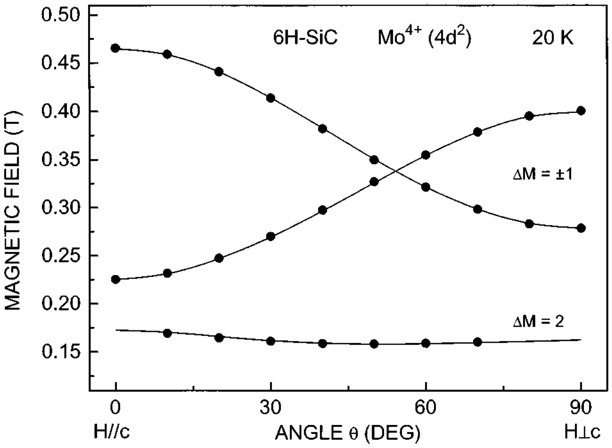

FIG. 2. Angular dependence of the two $\Delta M = \pm 1$ fine-structure ESR lines of Mo^{4+} $(4d^2)$. That of the forbidden transition $\Delta M = 2$, which is not observed under $H \| c$ and $H \perp c$, is also shown. The solid lines are computer fits, using numerical values for the spin-Hamiltonian parameters $g_\|$, $g_\perp$, and D, as quoted in the text.

ments $\mu = -0.63\mu_N$ for ^{99}Ru and $\mu = -0.69\mu_N$ for ^{101}Ru on the other hand, differ sufficiently, so that their hyperfine splitting should be resolved, at least for the outer $m_I = \pm 5/2$ components. This was not observed experimentally and we thus exclude ruthenium as candidate for the origin of the hyperfine sextet shown in the inset of Fig. 1. We are therefore left with molybdenum.

If the molybdenum impurity in its neutral state occupies a silicon-substitutional lattice site in 6*H*-SiC, its electronic ground state is the spin-only triplet $S = 1$ state $^3A_2$. Although this corresponds to tetravalent molybdenum, Mo^{4+} $(4d^2)$, this valency represents the neutral SiC semiconductor charge state. The spin-Hamiltonian[11] appropriate for a spin-triplet state $S = 1$ reads

$$\mathcal{H} = \mu_B g_\| H_z S_z + \mu_B g_\perp (H_x S_x + H_y S_y) + D\left\{ S_z^2 - \frac{1}{3} S(S+1) \right\},$$

where z denotes the c axis of the crystal. The D term is a measure of the axial crystalline electric field acting on the Mo^{4+} $(4d^2)$ ion. For the odd isotopes, ^{95}Mo and ^{97}Mo, the above Hamiltonian must be augmented by the characteristic hyperfine interaction operator $I\widetilde{A}S$. The electronic fine-structure term D in the above Hamiltonian accounts for a characteristic angular dependence of the two molybdenum ESR signals in Fig. 1, upon rotating the magnetic field H from $H \| c$ to $H \perp c$, as illustrated in Fig. 2. From a computer fit, the parameters of the above Hamiltonian were determined as follows:

$$g_\| = 1.9787 \pm 0.0013,$$

$$g_\perp = 1.9783 \pm 0.0013,$$

$$|D| = (3.32 \pm 0.01) \text{ GHz},$$

$$A_\|(^{95}\mathrm{Mo}) \approx A_\|(^{97}\mathrm{Mo}) = (92 \pm 2) \text{ MHz},$$

$$A_\perp(^{95}\mathrm{Mo}) \approx A_\perp(^{97}\mathrm{Mo}) = (92 \pm 2) \text{ MHz},$$

where $\mathrm{sgn}D = -\mathrm{sgn}A_\|, A_\perp$.

We should draw attention to an apparent lack of additional Mo^{4+} lines in the above ESR data: In 6*H*-SiC, there are *three* inequivalent lattice sites, viz. two quasicubic sites (k_1, k_2) and one hexagonal site (h). On either lattice site the local point symmetry is trigonal, C_{3v}. In view of this site multiplicity it is therefore surprising that ESR of Mo^{4+} $(4d^2)$ is observed for only one lattice site. This is in contrast to our previous findings for V^{3+} $(3d^2)$ and V^{4+} $(3d^1)$ in 6*H*-SiC, where ESR for all three lattice sites is observed.[1–3] Possibly, the ESR spectrum observed here arises from those molybdenum impurities, which occupy the most cubic, k_1, silicon site in 6*H*-SiC. On the other sites, k_2 and h, the axial crystalline electric field is much stronger and can thus lead to a much larger D parameter. This may impede an ESR observation of Mo^{4+} $(4d^2)$ on the k_2 and h site in 6*H*-SiC.

The ESR spectrum of Mo^{4+} $(4d^2)$ in 6*H*-SiC could not be observed at 77 K and above, in contrast to the ESR spectrum[1] of V^{3+} $(3d^2)$ in 6*H*-SiC and 4*H*-SiC. This can be explained by the greater spin-orbit coupling of Mo^{4+}, as compared to that of V^{3+}. Consequently, spin-lattice relaxation of the Mo^{4+} ion will be faster than that of V^{3+}. On the other hand, the ESR spectra of both Mo^{4+} $(4d^2)$ and V^{3+} $(3d^2)$ in 6*H*-SiC are readily saturated at liquid-helium temperatures, under elevated microwave power. This is a consequence of their common spin-only ground state $^3A_2$.

We finally mention that the ESR spectrum of Mo^{4+} $(4d^2)$ could also be detected in *n*-type bulk 6*H*-SiC wafer material obtained from CREE Research Inc.[10] This finding underlines that molybdenum is a likely trace impurity in SiC. The Mo^{4+} $(4d^2)$ concentration in the type (a) samples lies in the 10^{15} cm^{-3} range, whereas the Mo concentration in the type (b) samples is at least an order of magnitude less. The ESR spectrum of Mo^{4+} $(4d^2)$ could not be observed in *p*-type bulk 6*H*-SiC wafer material.

B. Trivalent molybdenum, Mo^{3+} $(4d^3)$

In *n*-type 6*H*-SiC we observed an additional ESR signal, which shows a strong angular dependence, see Fig. 3. This signal could be detected in both type (a) and type (b) samples. The defect responsible is clearly molybdenum correlated, since the ESR line is again flanked by hyperfine structure satellites, showing hyperfine-to-central line intensities of $(26 \pm 3)\%$ to $(74 \pm 3)\%$, which is in good agreement to the natural abundance of odd and even isotopes of molybdenum. The hyperfine satellites are shown under higher resolution in the inset of Fig. 3. The angular dependence of this signal is that of a center having fictitious spin $S' = 1/2$ and a highly anisotropic g' factor, according to $g'^2 = g_\|'^2 \cos^2\vartheta + g_\perp'^2 \sin^2\vartheta$, where ϑ denotes the angle between the static magnetic field H and the hexagonal c axis of the crystal. From a fit of the above relation to the experimental data we obtain

$$g_\|' = 1.945 \pm 0.001,$$

$$g_\perp' = 3.939 \pm 0.001,$$

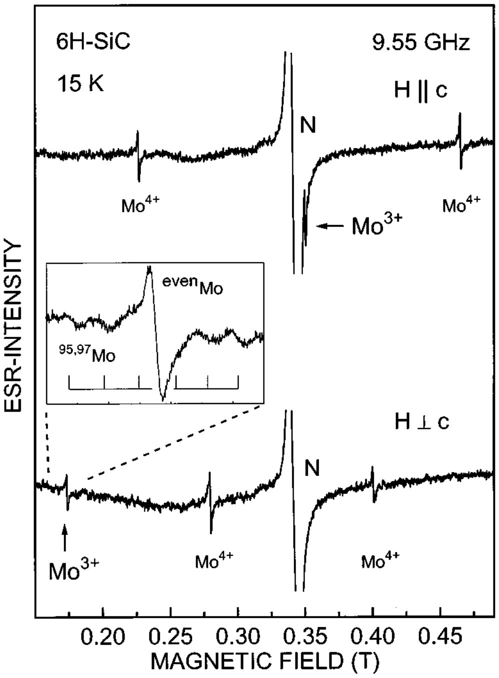

FIG. 3. Additional ESR signal observed in n-type $6H$-SiC, to be assigned to Mo^{3+} $(4d^3)$ under $H \| c$ (top) and $H \perp c$ (bottom). The dominant signal in the center arises from neutral nitrogen donors. The insert shows the hyperfine structure due to the odd isotopes ^{95}Mo and ^{97}Mo.

$$A'_{\perp}(^{95}\mathrm{Mo}) \approx A'_{\perp}(^{97}\mathrm{Mo}) = (73 \pm 2)\ \ \mathrm{MHz}.$$

The characteristics observed for the new single, molybdenum-correlated ESR signal are in line with its assignment to Mo^{3+} $(4d^3)$. Our arguments are as follows: If the Mo^{3+} $(4d^3)$ ion occupies a silicon site in SiC, its free-ion state ^{4}F will be split by the cubic-tetrahedral part of the crystalline potential into two orbital triplets, $^4T_2$ and $^4T_1$ and an orbital singlet, $^4A_2$, where $^4T_2$ is energetically lowest. The additional axial crystalline potential existing in the hexagonal $6H$ polytype of SiC will lead to an additional splitting of the $^4T_2$ state into an orbital doublet and an orbital singlet. *If* the orbital singlet state is energetically lower, a spin-only ground state $S=3/2$ for Mo^{3+} $(4d^3)$ results. The appropriate spin Hamiltonian is then identical to that given above for Mo^{4+} $(4d^2)$, $S=1$. However, for the $S=3/2$ ground state of $\mathrm{Mo}^{3+}(4d^3)$ the zero-field splitting, $W_{\pm 3/2} - W_{\pm 1/2} = 2D$, is at least $2\ \mathrm{cm}^{-1}$, since the $-1/2 \leftrightarrow -3/2$ fine-structure line has not been observed up to 1.7 T and therefore exceeds the energy of the microwave quantum, $h\nu \approx 9$ GHz, considerably. Under such conditions, i.e., for $2D \gg h\nu$, the $W_{\pm 1/2}$ state may be treated as a separate Kramers doublet, having fictitious spin $S'=1/2$, with[12]

$$g'_{\|} = g_{\|},$$

$$g'_{\perp} = 2g_{\perp}\left\{1 - \frac{3}{16}\left(\frac{h\nu}{2D}\right)^2\right\},$$

$$A'_{\|} = A_{\|},$$

$$A'_{\perp} = 2A_{\perp}\left\{1 - \frac{3}{16}\left(\frac{h\nu}{2D}\right)^2\right\}.$$

It is thus understood that the $g'_{\perp}$ factor is about twice that of $g'_{\|} = g_{\|} \approx 2$. A similar situation has been recently reported[7] to occur for Cr^{3+} $(3d^3)$ in $6H$-SiC and also, a long time ago, for V^{2+} $(3d^3)$ on trigonally distorted lattice sites in cubic ZnS.[13] Here, the $\langle 111 \rangle$ symmetry of the ESR spectra arises either from a static Jahn-Teller distortion or from association of the V^{2+} $(3d^3)$ ion with a nearby defect. The value of $g_{\perp}$ for the $S=3/2$ level from which $S'=1/2$ derives, was evaluated from a full diagonalization of $\mathcal{H}$ within the $S=3/2$ manifold, assuming $D > 2\ \mathrm{cm}^{-1}$. One obtains $g_{\perp} = 1.970 \pm 0.001$. Thus $g'_{\perp} = 2g_{\perp}$ within experimental error confirming that $h\nu/2D$ is negligibly small. We should finally mention that so far we could detect the ESR of Mo^{3+} $(4d^3)$ only for *one* of the three $(k_1,\ k_2,\ h)$ lattice sites in $6H$-SiC. As noted above, the same situation was found to occur for $\mathrm{Mo}^{4+}(4d^2)$. The reasons for this lack are still debated.

III. OPTICALLY DETECTED ELECTRON SPIN RESONANCE (ODESR)

In order to gain information about the excited electronic states of the Mo^{4+} $(4d^2)$ defect in $6H$-SiC we have performed magnetooptical investigations in the near-infrared spectral region. In particular, we have recorded the magnetic circular dichroism (MCD), which measures the difference in absorption for left-handed (σ_-) and right-handed (σ_+) polarized light propagating along a static magnetic field in the sample. The paramagnetic part of the MCD represents the magnetization of the defect's ground state, arising from thermal depopulation of its spin levels. If the depopulation is partially destroyed by resonant microwave saturation, ESR of the defect's ground state can be detected optically (ODESR), via its associated MCD spectrum.

The MCD and MCD-ODESR spectrometer system was the same as already used before in our studies of the neutral vanadium donor state $\mathrm{V}^{4+}(3d^1)$ in $6H$-SiC (Ref. 2) and $3C$-SiC (Ref. 5) and also of the ionized acceptor state V^{3+} $(3d^2)$ in $6H$-SiC.[3]

The type (a) samples show a strong MCD absorption in the spectral range 1.10-1.25 eV with several sharp zero-phonon lines (ZPL's), see Fig. 4. The MCD absorption of all of these ZPL's is dominated by a strong diamagnetic part and a weak paramagnetic part which can be used for an ODESR experiment. Six of these ZPL's are unambiguously assigned to Mo^{4+} $(4d^2)$ since the ODESR of Mo^{4+} is observed if the detection system is tuned to either of these lines. A corresponding ODESR spectrum is shown in Fig. 5. The strong ODESR at 750 mT is most likely due to boron acceptors caused by a broad boron-related MCD band underlying the Mo^{4+} ZPL's.

The remaining MCD ZPL's show no Mo-correlated ODESR since they are either completely diamagnetic or give rise to ODESR signals which are too weak or outside the accessible magnetic field range. However, they originate most likely from Mo^{4+} located on the remaining inequivalent Si lattice sites k_2 and h, which are expected to have a

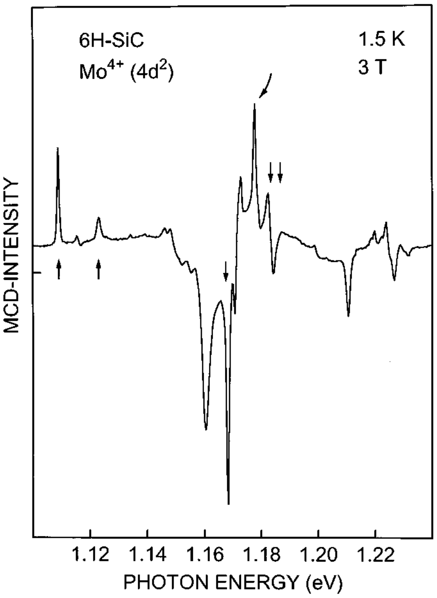

FIG. 4. MCD absorption of Mo^{4+} $(4d^2)$ in a $6H$-SiC substrate. The ZPL's marked with arrows reveal ODESR spectra of the type shown in Fig. 5.

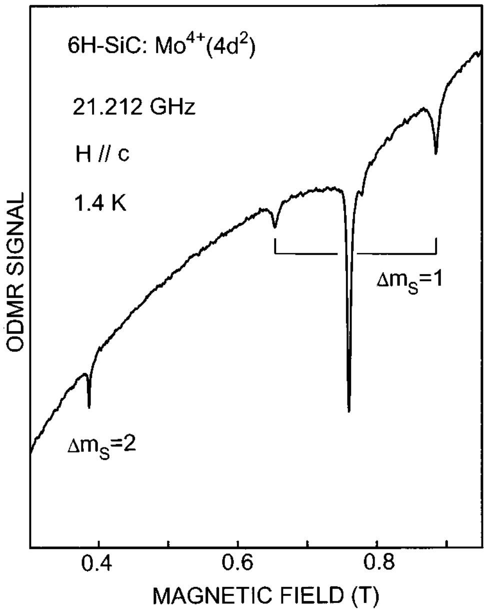

FIG. 5. ODESR spectrum detected on the 1.169 eV Mo^{4+} $(4d^2)$ MCD line of Fig. 4.

larger axial field splitting of the $^3A_2$ ground state and therefore might not show a paramagnetic MCD.

We assign the Mo^{4+} $(4d^2)$ MCD absorptions of Fig. 4 to the $^3A_2 \rightarrow {}^3T_2$ crystal-field transition, from which a cubic crystal field splitting constant of $Dq = -926\ \mathrm{cm}^{-1}$ is deduced. The excited $^3T_2$ crystal field state is split by the large spin-orbit interaction and the trigonal field resulting in six MCD ZPL's for each of the three lattice sites in $6H$-SiC, which is consistent with the six MCD ZPL's which could be assigned to $Mo^{4+}(4d^2)$ on one inequivalent lattice site. A more extensive study of these findings will be published elsewhere.

IV. ELECTRICAL ACTIVITY OF MOLYBDENUM IN SiC

This work has shown that Mo_{Si} in $6H$-SiC can occur in two charge states. Consequently, this impurity is electrically active as an acceptor, presumably as a deep-level defect. The tetravalent valency Mo^{4+} corresponds to the neutral state, whereas the trivalent valency Mo^{3+} represents the ionized acceptor state, according to $A^-/A^0 \triangleq Mo^{3+}/Mo^{4+}$. Such an assignment is in line with our finding, that ESR of Mo^{3+} could only be observed in n-type material. In p-type SiC, no ESR of these A^- states is expected. The determination of the $(-/0)$ acceptor level of molybdenum in $6H$-SiC by adequate techniques, such as photo-ESR and junction spectroscopy, remains as an important task for future studies.

It should also be mentioned that molybdenum is a very promising contact material for high-temperature devices.[14] Our results suggest that the formation of deep acceptor levels in SiC caused by Mo diffusion at high operation temperature might result in a long-term degradation of devices using Mo contacts.

V. SUMMARY

Using ESR and ODESR techniques we have demonstrated that the $4d$ element molybdenum is a common, silicon-substitutional trace impurity in $6H$-SiC crystals, as was found before for the $3d$ elements vanadium and titanium. From the observation of two charge states, Mo^{4+} $(4d^2)$ and Mo^{3+} $(4d^3)$, we conclude that this impurity must act as a deep-level acceptor. Consequently, Mo-trace impurities must be taken into account when analyzing electrical compensation processes in silicon carbide.

ACKNOWLEDGMENT

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[1] K. Maier, H. D. Müller, and J. Schneider, Mater. Sci. Forum **83-87**, 1183 (1992), and references therein.

[2] M. Kunzer, H. D. Müller, and U. Kaufmann, Phys. Rev. B **48**, 10 846 (1993).

[3] M. Kunzer, U. Kaufmann, K. Maier, and J. Schneider, Mater. Sci. Eng. B **29**, 118 (1995).

[4] K. F. Dombrowski, U. Kaufmann, M. Kunzer, K. Maier, J. Schneider, V. B. Shields, and M. G. Spencer, Appl. Phys. Lett. **65**, 1811 (1994).

[5] K. F. Dombrowski, U. Kaufmann, M. Kunzer, K. Maier, J. Schneider, V. B. Shields, and M. G. Spencer, Phys. Rev. B **50**, 18 034 (1994).

[6] M. Feege, S. Greulich-Weber, and J.-M. Spaeth, Semicond. Sci. Technol. **8**, 1620 (1993).

[7] P. G. Baranov, V. A. Khramtsov, and E. N. Mokhov, Semicond. Sci. Technol. **9**, 1340 (1994).

[8] P. G. Baranov and N. G. Romanov, Mater. Sci. Forum **83-87**, 1207 (1992).

[9] Yu. A. Vodakov, E. N. Mokhov, M. G. Ramm, and A. D. Roenkov, Krist. Tech. **6**, 729 (1979).

[10] CREE Research Inc., Durham, NC 27713.

[11] See, e.g., A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[12] G. W. Ludwig and H. H. Woodbury, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 223. Note that Eq. (7.6) in this review has an incorrect sign.

[13] J. Schneider, B. Dischler, and R. Räuber, Solid State Commun. **5**, 603 (1967).

[14] C. Jacob, S. Nishino, M. Mehregany, J. A. Powell, and P. Pirouz, *IOP Conference Series* Vol. 137 (IOP, Bristol, 1994), p. 247.