Pulsed EPR and ENDOR Study of SiC Nanopowders

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In this work field-sweep electron spin echo and pulsed electron nuclear double resonance study of the silicon carbide (SiC) nanoparticles (np-SiC) of different sizes is presented. Nitrogen (N) triplet lines due to the isolated N donor state was observed in np-SiC with grain size $d > 100$ nm. With a decrease of the particle size up to 50 nm the N triplet lines transforms into one single exchange line due to the delocalization of the donor wave function caused by the size confinement effect. Along with N donors the carbon vacancy (V_C) located in cubic phase was observed in np-SiC with $d < 100$ nm. The further decrease of the grain size to $d < 50$ nm leads to the appearance of the V_C located in hexagonal crystalline phase and carbon dangling bonds located in the carbon excess phase of np-SiC. The fact that only N donor center at "k2" quasi-cubic position substituting Si site was observed in the field-sweep electron spin echo and pulsed electron nuclear double resonance spectra of np-SiC was explained by high compensation degree of the samples and the presence of carbon excess in np-SiC. The appearance of the proton electron nuclear double resonance signal in no-SiC with $d < 100$ nm indicates that the hydrogen retention in np-SiC increases with decreasing of grain size.

1. Introduction

The semiconductor industry requires the development of new materials to meet the needs of rapid RF circuits, optical devices, data storage, and energy saving solutions for lighting. Furthermore, nanotechnology-based approaches target the production of nanostructured materials required to make progress in the scaling-down of electronics and for photonic devices. Nanoparticles of various materials such as metals, semiconductors, and oxides have been studied extensively because of their unique physical and/or chemical properties, which are different from those of bulk materials. Their unique properties result from quantum size effect, interface, and/or surface effect. The structure devices, made by using nanosized silicon carbide (np-SiC) powders, have high hardness; high wear resistance and good self-greasing effect, high thermal conductivity, low thermal expansion efficient and high temperature strength, etc. The great potential of the np-SiC for future applications in spintronics stimulates detailed studies of the effects of impurities and defects in their electronic properties. In particular, np-SiC material doped with nitrogen (N) atoms is an important issue to be investigated, since N donors are common contaminants in SiC bulk, acting as n-type dopant. Although N has been found to be present in the nanomaterials, there is no experimental evidence indicating for the formation of the shallow donor state of N in np-SiC. One of the reason of this fact might be passivation of N donors by hydrogen, which can be introduced by final

etching of the np-SiC [1]. The present study provides the first information about the formation of the shallow N donor state in np-SiC and impacts of the hydrogen and intrinsic defect formation on its electronic properties.

2. Experimental details

The non-stoichiometric (C/Si > 1) np-SiC samples with $d \leq 50$ nm were obtained by self-propagating synthesis of carbon (C) and highly active silicon (Si) at $T = 1250\,°C$ [2], while np-SiC with 50 nm $< d <$ 100 nm were commercially produced. The nonstoichiometric (C/Si > 1) green/black np-SiC with $d > 100$ nm were produced in an electric resistance type furnace at $T = 1750\,°C$ with quartz sand and petroleum coke as its main raw materials. The X-band ($\nu = 9.7$ GHz) two pulse field-sweep electron spin echo (FS ESE) spectra and pulsed electron nuclear double resonance (ENDOR) spectra in Davies and Mims pulse sequences were measured on Bruker ELEXSYS E580 spectrometer at $T = 6$ K.

3. Results and discussion

Figure 1 shows the X-band FS ESE spectra measured in np-SiC at 6 K. The np-SiC with $d > 100$ nm revealed triplet lines due to the nitrogen (^{14}N, $I = 1$, 99.6%) donors having $S = 1/2$ and single line coincided with the central triplet line of N.

The ^{14}N triplet line of significantly lower intensity than that was observed in np-SiC with $d > 100$ nm was also observed in np-SiC with 50 nm $< d <$ 100 nm. With the decrease of particle size the intensity of the central line increases and it consists of the two unresolved components. Only the central line with two unresolved components was observed in np-SiC with $d < 50$ nm. The reduction
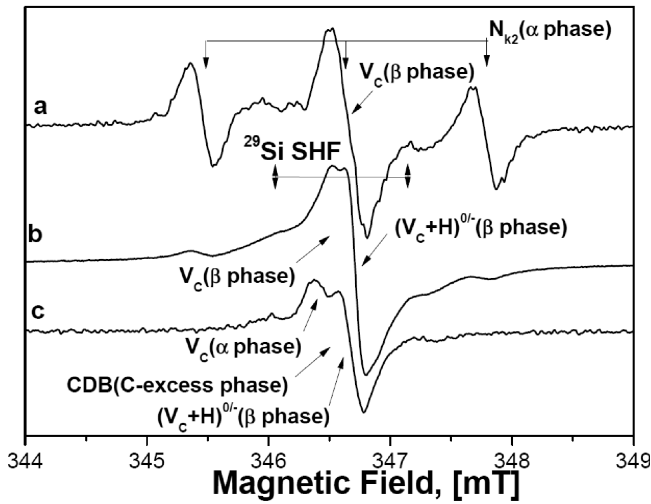
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Fig. 1. The X-band first derivative of FS ESE measured in np-SiC with $d > 100$ nm (a), 50 nm $< d <$ 100 nm (b), $d < 50$ nm (c) at $T = 6$ K.

in intensity of the ^{14}N hyperfine lines originating from isolated N donors with the decrease of the particle size can be explained by the size confinement effect. The decrease of the particle size leads to the delocalization of the donor wave function and as a result the overlap between wave functions of neighboring donors was increased.

The similar behavior was observed in nanocrystalline silicon (Si) for phosphorus donors with the decrease of particle size [3]. With the decrease of nanoparticle size ^{14}N triplet lines transforms into one single exchange line coincided with the central line of ^{14}N triplet. However, owing to the short spin–lattice relaxation time this single line caused by exchange interaction between N donors cannot be observed in the FS ESE spectrum of np-SiC. On the other hand the observation of exchange line in continuous wave EPR spectrum of np-SiC is hampered by the presence of several additional unresolved EPR signals coincided with the central ^{14}N triplet line at X-band frequencies. The EPR measurements at higher microwave frequencies have shown the broadening of the signal that consists of a several unresolved lines and as a result did not give the advantage over the X-band.

The parameters of the single lines deduced from the simulation of the FS ESE spectra observed in np-SiC along with their identification were given in Table. The identification of the additional single lines observed in the FS ESE spectrum of np-SiC was undertaken by comparison of their experimental EPR parameters with those obtained for the defects previously observed in np-SiC [2].

As can be seen from Table, three different paramagnetic intrinsic defects were presented in np-SiC material. The presence of the superhyperfine lines due to the interaction with ^{29}Si nuclei ($I = 1/2$, 4.7 %) symmetrically located with respect to the central line at $g = 2.0029(3)$ with $A_{\rm iso} = 29.7$ MHz gives us evidence to assign it with a carbon vacancy (V_C) in the cubic

phase [2]. The second defect at $g_{\rm iso} = 2.0041(3)$ was attributed to the V_C in hexagonal phase [2, 4]. The third line at $g_{\rm iso} = 2.0031(3)$ was attributed to the sp^3-coordinated carbon dangling bonds (CDB) located in the carbon excess phase of np-SiC [2].

EPR parameters of paramagnetic centers observed in np-SiC.

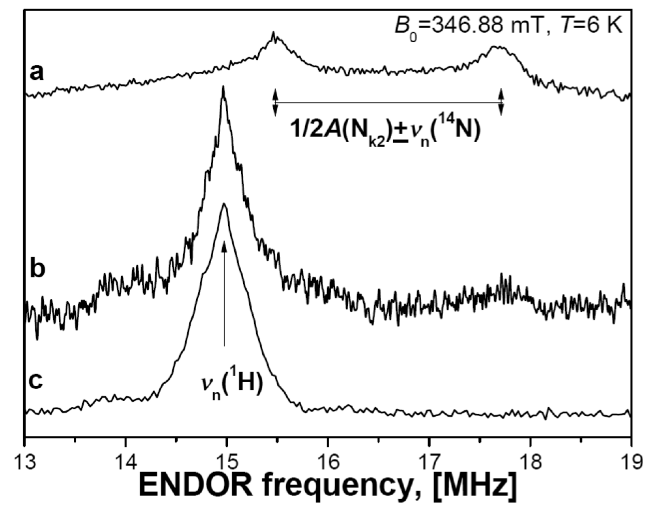| d [nm]	Center (phase)	$g_{\|\|}$	$g_{\perp}$	Ref.
> 50	N_{k2} (α-SiC)	2.0037(3)	2.0030(3)	[1]
		$A_{\|\|}$=1.19 mT	$A_{\perp}$=1.19 mT	
	V_C (β-SiC)	2.0029(3)	2.0029(3)	[2,4]
< 100	$(V_C+H)^{0/-}$ (β-SiC)	2.0028(3)	2.0028(3)	[2]
$\leq$ 50	sp^3-coordinated CDB (C — excess)	2.0031(3)	2.0031(3)	[2]
	V_C (α-SiC)	2.0041(3)	2.0041(3)	[2,4]

Fig. 2. The X-band pulsed ENDOR spectra measured on the central FS ESE line in np-SiC with $d >$ 100 nm (a), 50 nm $< d <$ 100 nm (b), $d < 50$ nm (c) at $T = 6$ K.

Figure 2 shows ENDOR spectra measured at the central FS ESE line position in np-SiC with $d > 100$ nm and 50 nm $< d < 100$ nm. Only one doublet lines due to ^{14}N nuclei corresponding to the transitions $1/2A_i \pm \nu_{\rm n}(^{14}$N) ($\nu_{\rm n}(^{14}$N) — nuclear Larmor frequency of ^{14}N) with hyperfine interaction (hfi) constant $A = 33.32$ MHz were observed in the ENDOR spectrum of np-SiC with $d > 50$ nm. The observed ENDOR spectrum with hfi constant 33.32 MHz corresponds to the nitrogen donor center N_{k2} substituting "k2" quasi-cubic position in 6H SiC lattice [5, 6]. The ENDOR lines due to the N substituting quasi-cubic "k1" (N_{k1}) and hexagonal "h" (N_h) positions were not found in the ENDOR spectrum of np-SiC. One of the reasons is that V_C presented in np-SiC gives rise to the compensation of the sample. Indeed, N_h has a substantially more shallow energy level (81.04 meV) than that of N_{k1} and N_{k2} and as a result its level is not oc-

cupied in compensated samples. At the same time the absence of the lines due to the N_{k1} center in ENDOR spectrum cannot be explained by compensation effect because it has the energy level (137 meV) close to that of the N_{k2}. Even in highly compensated samples the triplet lines due to the N_{k2} center was observed in the EPR spectrum of 6H SiC wafers along with N_{k1} center but with different intensity ratio [7].

In accordance with recent pulsed ENDOR and general TRIPLE ENDOR data the N_{k2} with deeper energy level 142 meV was attributed to the N donors substitute Si site [6]. This fact gives the argument to suggest that the absence of the N_{k1} substituting C site is caused by technology preparation of the np-SiC rather than by compensation effect. Indeed, in accordance with the site-competition principle proposed in [8], the C-excess in 6H SiC inhibits the site competition process between nitrogen and carbon for C sites and therefore may provoke the N incorporation on Si site.

As can be seen from Fig. 2b,c, the ENDOR spectra measured at the FS ESE position of V_C center in np-SiC with $d < 100$ nm is centered on the hydrogen (^{1}H) nuclear Zeeman frequency. To our knowledge firstly in SiC the ^{1}H ENDOR spectra were observed in a-SiC:H alloy in [9].

The presence of the ^{1}H ENDOR signal in np-SiC samples indicates the existence of hydrogenated regions in the samples and possibly can be caused by final etching of the np-SiC in hydrofluoric acid [2]. Previously based on the analysis of the ^{1}H hfi couplings it was suggested that ^{1}H is weakly coupled with V_C forming the hydrogen-related defect (V_C+ H) [2]. At the same time in np-SiC with $d > 100$ nm no ^{1}H signal was observed in ENDOR spectrum measured at the central FS ESE triplet line position which coincided with V_C center. This fact allows to conclude that H incorporation in np-SiC depends on the particle size. This conclusion agrees well with the correlation between diamond grain size and H retention found in diamond films [10]. The H retention in diamond films increases with decreasing grain size, and suggest that H is bonded and trapped in nanodiamond grain boundaries and on internal grain surfaces. Thus, we may consider that the incorporation of H in np-SiC is grain size dependent.

4. Conclusions

The N donor center substituting quasi-cubic position with deeper energy level in the band gap at 142 meV (N_{k2}) and three types of intrinsic defects, including carbon vacancy located in the hexagonal and cubic crystalline phase, CDB located in the carbon excess phase have been revealed in the FS ESE spectrum of np-SiC.

With decrease of the particle size the N donors exhibit size confinement effect which leads to the delocalization of the donor wave function and as a result owing to the overlap between wave functions of neighboring donors the N triplet line transforms into the one single exchange line. The onset of the size confinement effect was found to be $d < 50$ nm in np-SiC. The fact that only one N_{k2} donor center was observed in the FS ESE and pulsed ENDOR spectra of np-SiC was explained by high compensation degree and technology preparation of the sample. The energy level of N_h canter (81.04 meV), which is a substantially shallower than that of N_{k1} and N_{k2} centers, is not occupied in compensated np-SiC samples. The absence of the N_{k1} center with energy level close to the N_{k2} center (137 meV) can be explained by the deviation of stoichiometry towards C in np-SiC samples.

The appearance of the ^{1}H ENDOR signal in np-SiC, indicates that incorporation of hydrogen in SiC nanomaterials is grain size dependent. The H retention in np-SiC increases with decrease of grain size. The hydrogenation of the np-SiC was occurred when particle size becomes less than 100 nm.

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