Optical Properties of Vanadium and Nitrogen Doped 4H and 6H-SiC

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***Abstract* – Linear optical properties of vanadium (V) and nitrogen (N) doped single-crystal sub-millimeter wafers of 4H-SiC and 6H-SiC grown for industrial applications in optics and electronics are studied in detail within transparency window and from 0.2 THz to 2.1 THz range to reveal usability in parametric frequency conversion. Manufactured wafers are found not uniform in polytype composition. Optical properties of majority of wafers indicated applicability for THz wave generation by optical rectification method. The wafers demonstrated large optical damage threshold exceeding that for widely used crystals GaSe at least for from 3 to 5 times and up to 10 times lower (from a few tens to below 1 cm^{-1}) absorption coefficient in the THz range. Birefringence of doped 4H-SiC are still close to that for pure crystals, i.e. suitable for phase matched frequency conversion within the transparency window or into the THz region. Polytype 6H seems suitable for phase matched down-conversion into the THz range. Nevertheless, absolute values of refractive indices are seriously varying wafer to wafer.**

***Index Terms* – Silicon Carbide, THz, optical damage threshold.**

I. Introduction

In RECENT years, high-purity single-crystal SiC has found applications in a number of cutting-edge technologies including optics and semiconductor electronics. There are over 250 crystalline forms of SiC [1]. Hexagonal silicon carbide (H-SiC) is a wide bandgap semiconductor crystal belonging to the point group symmetry $C_{6v}^4 - P6_3mc$ –and has positive birefringence ($n_e > n_o$). It is one of the hardest high-performance materials available, second only to diamond; and it possesses superior resistance to harsh environments, such as high temperature and pressure. The different polytypes of H-SiC are variations of the same chemical compound that are identical in two dimensions and differ in the third. Thus, they can be viewed as layers stacked in a certain sequence, or combinations of two stacking sequences, with a periodicity of N double layers (NH-SiC) in the stacking direction [2, 3].

Of these, the hexagonal polytype 4H-SiC (N = 4) and 6H-SiC (N = 6) have been found to be the most suitable for a wide variety of applications. They also have the important advantage in that they can be grown as large single-crystal boules of very high optical quality with maximum a few micro defects. The main transparency window of 4H-SiC was found to extend between 0.37 μm to 5.6 μm [4]. It is suitable for phase matched parametric frequency conversion within it [4], as well for down-conversion into the THz region demonstrating here unmeasurable low coefficient of optical losses [5]. Polytype 6H-SiC is not phase matchable within maximal transparency window 0.4 μm to 5.7 μm [4], but it possesses enough high birefringence for down-conversion into the THz range due to decreasing of the relative contribution of the THz wave vector $\boldsymbol{k}_1$ in the $\boldsymbol{k}$-vector sum in phase matching condition [6]. High transparency was reported in 6H-SiC at 0.5 THz to 3 THz [7] and between 40 μm to 120 μm (2.5 THz to 7.5 THz) [8]. So, anyway it can be used for THz wave generation at least by optical rectification method that already was demonstrated [7].

Unidentified polytype demonstrated a high optical damage threshold – up to 80 GW/cm^2 under excitation by 10 ns pulses from an Nd:YAG laser at 1.064 μm [2]. 4H-SiC and 6H-SiC crystals also possess a range of other attractive physical properties that are responsible for efficiency of parametric frequency conversion processes. A summary of SiC properties for various polytypes and a bibliography of the available literature can be found on [9].

II. Problem Definition

Doped SiC crystals with modified properties are widely produced all over the world for application in optics and electronics. Modified crystals can have high or even improved potential for application in parametric frequency conversion to that in undoped SiC. Despite this, a very little work is done on properties study of doped SiC [10] – [12]. To the best of our knowledge, no study was carried out on THz properties. It should be outlined that optical properties only for o-wave can be studied due to the widespread prevalence of SiC wafers cut orthogonally to the crystal optical axis. A grown single crystal SiC can contain a mixture of polytypes [13, 14] and other undesirable properties.

In this work, we experimentally studied optical properties of vanadium (V) doped crystals 4H-SiC and 6H-SiC grown for applications in linear optics and nitrogen (N) doped for applications in electronics.

III. Experimental Setup

In total, optical properties of 19 4H-SiC and 6H-SiC samples of two orientations (<0001> and <1120>; cutting accuracy ±0.5°) were studied at room temperature. The

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samples were wafers cut and finished by Shanghai Doheng Optics and Fine Mechanics Co., Ltd. (China) [15] from standard V and N doped SiC ingots of 100 mm diameter grown by MOCVD method for industry application in, respectively, optics and electronics. The wafers were from 120 to 310-μm thick and faced by 10 × 10 mm (in rear case by 5 × 10 mm). Wafer (labeled as 4H-3, 4 and 6H-3, 4) orientations made possible measurement ordinary (*o*) and extraordinary (e) wave absorption coefficients. Direction <1120> is, within about 2°, orthogonal to optical axis <0001>. Side directions of these wafers were cut along the direction of ***x*** and ***y***-axes. If polarization of the probing beam parallel to side 1 or side 2, it was identified by additional abbreviation 0° or 90°. This type single wafers allowed to measure optical properties of both o and e-polarized waves, as well as to check cutting accuracy by using crossed polarizers. Parameters of manufactured wafers are listed in Tab. I.

TABLE I
LABELS AND PROPERTIES OF SELECTED SIC WAFERS

Orientation		<0001>				<1120>			
SiC label		4H-1	4H-2	6H-1	6H-2	4H-3	4H-4	6H-3	6H-4
Thickness, μm		299	125	348	130	310	128	288	130
Bandgap, eV		3.02	3.02	3.02	3.02	3.29	3.29	3.02	3.02
Admixture absorption peaks, nm		–	–	–	–	~600	~600	~950	~950
Raman freq, cm^{-1}	90°	171, 254, 570, 770, 785, 797, 965		149, 266, 505, 513, 767, 788, 966		203, 264, 610 777, 783, 798, 966		149, 240, 266, 505, 513, 767, 788, 798,	
	0°					264, 609, 783, 798, 839, 969		240, 505, 787, 798, 889, 970	

Shimadzu Sequential X-ray Fluorescence Spectrometer Lab Center XRF-1800 (Japan) was used for composition analyses.

The transmission spectra of the manufactured wafers in nonpolarized and polarized light were recorded by spectrometer Cary 5000, Varian: operation range is from 190 nm to 3200 nm, spectral resolution 0.1 nm. Film polarizers (LOMO, Russia for 400…750 nm range) were used in the second case. IR spectra were recorded by IR-Fourier spectrometer Tensor 27, Bruker: operation range from 7000 cm^{-1} to 375 cm^{-1}, spectral resolution 4 cm^{-1}.

Measurements at 0.1 THz to 2.1 THz were performed using a homemade time-domain spectrometer (TDS). A compact femtosecond Er-doped fiber laser (Toptica Photonics, Germany) is used as a pump source with the average power of 100 mW at 775 nm after the second harmonic generation module. The duration of laser pulses is about 100 fs. Pulsed terahertz radiation is generated from the surface of a p-type InAs semiconductor. It is optically polished, thinned to 200 μm and placed in the magnetic field of a lightweight permanent magnetic system in order to enhance the efficiency of the optical-to-terahertz conversion. The generated terahertz radiation is transmitted through a THz low-pass filter to filter out residual red light in the pump arm of the spectrometer and then passes through a THz polarizer (Tydex, Russia). It is then collimated by an off-axis parabolic mirror and focused onto a sample using a TPX lens. The terahertz beam waist is less than 5 mm in diameter at the sample position. The terahertz radiation passed through the sample and collected by a similar mirror. The main detecting element is a (110)-cut ZnTe crystal. Other details are presented elsewhere [16].

Vibration scattering spectra were studied by using Raman Spectrometer inVia (Renishaw, UK) under excitation by polarized emission of semiconductor lasers operating at 785 nm at the wavenumber range down to 100 cm^{-1}.

Optical damage threshold was established by transmission deviation from the linear trend under increasing intensity pump beam. Fundamental and SHG of Nd:YAG laser LS-2132UTF (Lotis, Belarus) were used as the pump sources. The fundamental output wavelength is 1.064 μm, pulse duration 6.8 ns. Pump intensity was controlled by polarizer rotation on the laser output and crystal positioning after spherical lens with focusing length $f = 30$ cm.

IV. EXPERIMENTAL RESULTS

Chemical composition of SiC samples is found stoichiometric. We were not able to determine impurity contents.

Then, to identify wafer polytypes, short wavelength edges/energy bandgaps of SiC wafers were determined. Energy bandgap was calculating by using relations [17, 18]:

$$(\alpha h\nu)^{1/r} \propto h\nu - E_g \,,$$

$$h\nu = \frac{ch}{\lambda} \cdot 10^9 \,,$$

where α is an absorption coefficient, $h\nu$ is a quant energy in eV, E_g is a bandgap, r is a coefficient determined by the type of electric conductivity, c is the light speed (in meters per second), h is the Plank constant, (eV×sec), λ is wavelength in nm. Absorption coefficients for o and e-wave α_{ieo} were estimated from recorded transmission spectra $T_i(\lambda)$ of the wafers with thickness d_i (Tab. I) as:

$$T_i(\lambda) = \frac{(1 - R_i(\lambda))^2 e^{-\alpha_i d_i}}{1 - R_i(\lambda)^2 e^{-\alpha_i d_i}} \,, \tag{1}$$

from whence:

$$\alpha_i(\lambda) = -\frac{1}{d_i} \ln\left(\sqrt{A^2 + \frac{1}{R_i(\lambda)^2}} - A\right), \tag{2}$$

where A is:

$$A = \frac{(1 - R_i(\lambda))^2}{2T_i(\lambda) R_i(\lambda)^2} \,.$$

Here R_i is a Fresnel refraction coefficient

$$R_i(\lambda) = \frac{(n_i(\lambda)-1)^2}{(n_i(\lambda)+1)^2}, \quad (3)$$

where $n_i(\lambda)$ are known refractive indices for 4H-SiC determined by dispersion equations [5]:

$$n^2_{o-4H}(\lambda) = 9.90 + \frac{0.1364}{\lambda^2 - 0.0334} + \frac{545.0}{\lambda^2 - 163.69}, \quad (5)$$

$$n^2_{e-4H}(\lambda) = 10.52 + \frac{0.1701}{\lambda^2 - 0.0258} + \frac{729.2}{\lambda^2 - 194.72} \quad (6)$$

with validity range from 0.37 μm to 1000 μm and 6H-SiC [4]:

$$n^2_{o-6H}(\lambda) = 6.5723 + \frac{0.1401}{\lambda^2 - 0.03178} - 0.02153\lambda^2, \quad (7)$$

$$n^2_{e-6H}(\lambda) = 6.7452 + \frac{0.15352}{\lambda^2 - 0.03597} - 0.02249\lambda^2 \quad (8)$$

with validity range from 0.4 μm to 2.3 μm.

In this work, bandgaps were also calculated by using measured optical density D_i from relation [13]:

$$\sqrt{D_i h\nu} \propto h\nu - E^i_g, \quad (9)$$

that can be exploited for indirect semiconductors, like SiC. Transmission T and optical thickness D are related as:

$$T(\lambda) = 10^{-D(\lambda)}. \quad (10)$$

Estimated bandgaps are shown in Fig. 1.

Selected Raman scattered spectra are depictured in Fig. 2.

Raman scattering spectra scaled up in the spectral range from 750 cm^{-1} to 850 cm^{-1} for selected wafers are shown in Fig. 3.

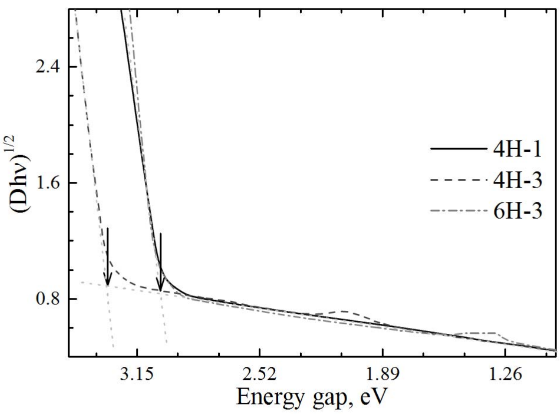
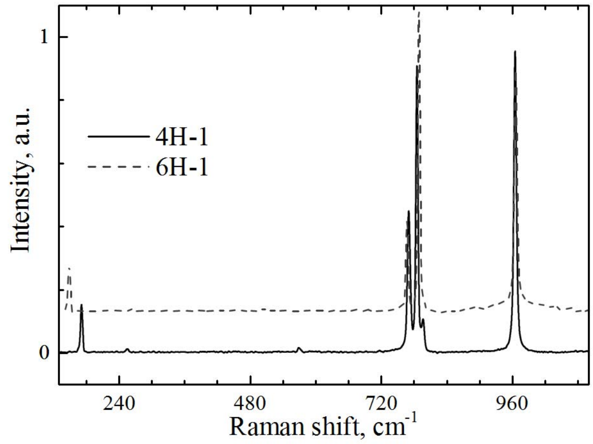
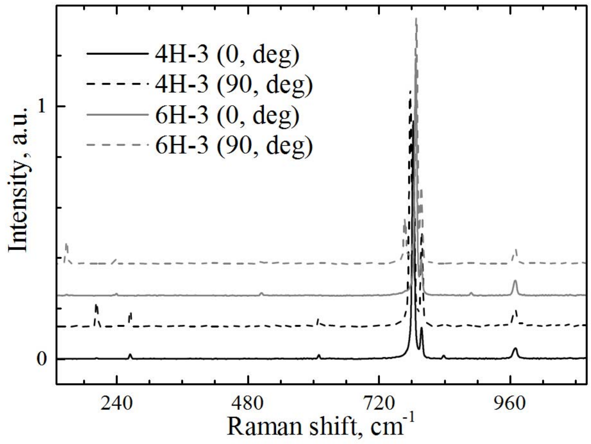


Fig. 1. Typical energy bandgaps of wafers: 4H-1, 4H-3, 6H-3.



(a)



(b)

Fig. 2. Raman spectra: backscattered in wafers 4H-1 and 6H-2 (a), and scattered at different angles shown in the figure insets in wafers 4H-3 and 6H-3 (b).

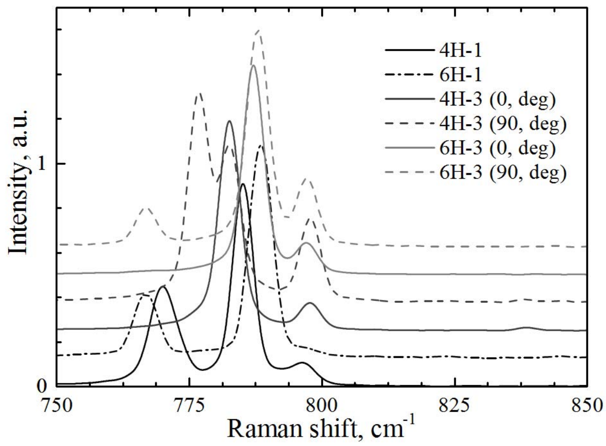
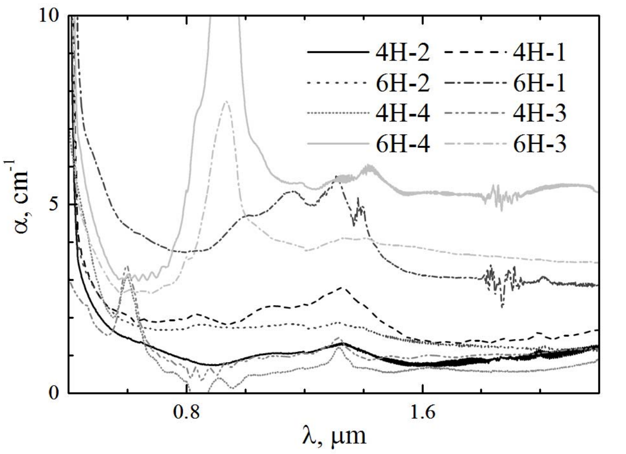


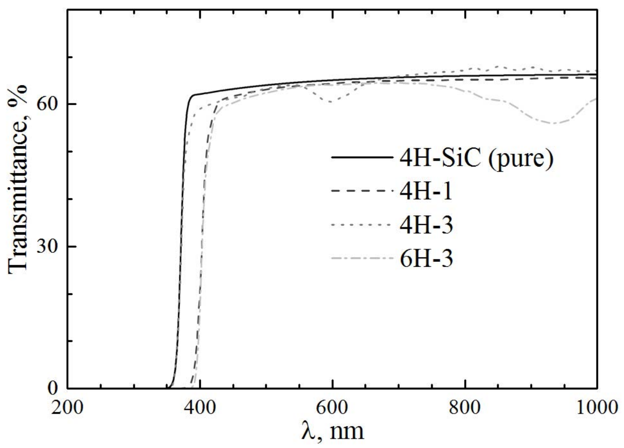
Fig. 3. Detailed Raman scattering spectra for selected wafers identified in the figure insets.

Absorption coefficient spectra are presented in Fig. 4.

Fig. 5 exhibits optical properties for selected wafers in the THz region.



(a)



(b)

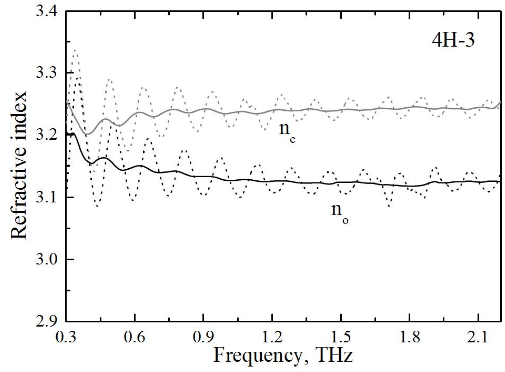
Fig. 4. Absorption coefficient spectra for (a) wafers under the study that are identified in the figure inset and (b) their transmission edge and transmission edge of a high optical quality (2 micropipe/cm^2) 350-μm thick 4H-SiC wafer.

It was found that optical damage threshold is strongly depending on the intensity of N-induced absorption peak and drops from 140 MW/cm^2 for V-doped wafers down to 85 MW/cm^2 for the wafer with the most intensive N-admixture peak.

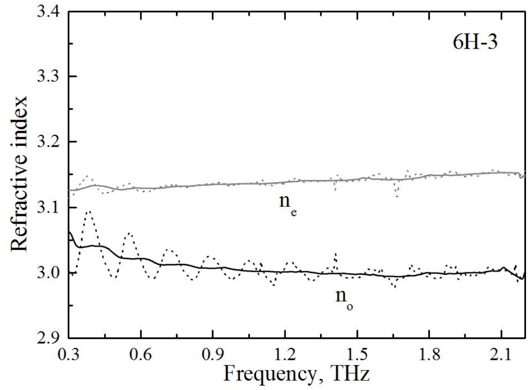
V. Discussion of Results

We were not able to determine impurity contents, as it was already reported for materials doped with not isovalent impurities [19] or impurities that does not form chemical compound identical in structure to parent material [20]. However, low doping by such type impurities is leading to significant changes in physical properties of parent crystals. To estimate doping effect, polytype structure of the wafers should be preliminary identified.

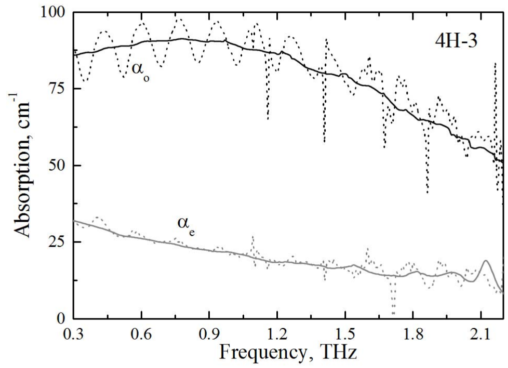
It was found that recorded spectra (Fig. 4) are identical for some pairs of SiC wafers: 4H-1 and 4H-2, 4H-3 and 4H-4, 6H-1 and 6H-2, 6H-3 and 6H-4. On the other hand, it comes



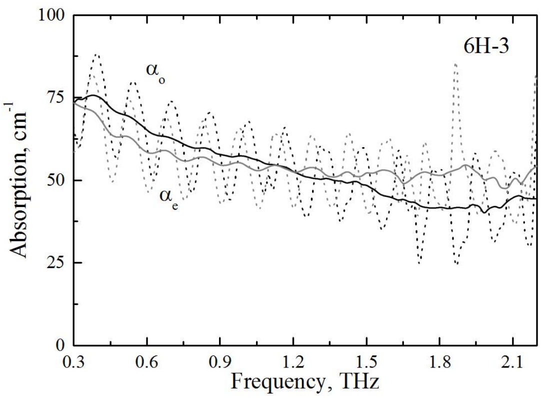
(a)



(b)



(c)



(d)

Fig. 5. Dispersion of refractive indices and absorption coefficients in wafers: (a, c) 4H-3 and (b, d) 6H-3.

from Fig. 2 that Raman scattering spectra for wafer 4H-1 is sooner like that for 6H-1 & 6H-4 that shows identity of their structures. Difference in structures is also coming from bandgap data in Fig. 1.

Optical absorption coefficient in the transparency window for all manufactured wafers never exceed 3…4 cm^{-1} mostly being about a few parts of cm^{-1} that is acceptable for nonlinear applications. Well resolved absorption peaks were observed in polarized light at 600 nm (4H-3, 4H-4) or 900 nm (6H- 3, 6H-4) (Fig. 4a). Similar peaks were observed elsewhere [21] – [24]. On the other hand, absorption peaks at 900 nm was recorded for o-wave in R15 polytype of SiC that possesses close structure to 6H-polytype [25]. Fortunately, these polytypes have different Raman spectra that can be used for identification. Only one wafer (6H-1, <0001>) has shown an absorption coefficient below 1 cm^{-1} in the THz region. The most usual coefficient is found to be about few tens of cm^{-1} rising to 350 cm^{-1} in a few cases that is much larger than that for pure SiC like optical damage threshold [5].

VI. Conclusion

Optical properties of vanadium (V) and nitrogen (N) doped single crystals of 4H and 6H polytype of SiC grown for industrial applications in, respectively, optics and electronics are studied in detail to reveal usability in parametric frequency conversion. It was established that doped SiC is not uniform in polytype composition. Most studied wafers indicated applicability for optical rectification, as a mean of THz wave generation, accounting large damage threshold exceeding that for widely used crystal GaSe for from 3 to 5 times. Besides, SiC wafers with optical absorption coefficient below a half of cm^{-1} in the visible region and 1 cm^{-1} in the THz range were found. It is up to 10 times lower to that of GaSe. Birefringence of doped 4H-SiC are still close to pure SiC crystals, i.e. suitable for phase matched frequency conversion within the transparency window or into the THz region. Polytype 6H is likely also suitable for phase matched down-conversion into the THz range. Nevertheless, absolute values of refractive indices are seriously varying wafer to wafer. It can be proposed that cooling is preferable in many cases to decrease optical losses and make all industrial samples useful for applications in frequency conversion.

Acknowledgment

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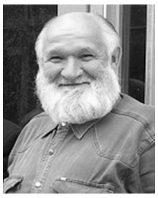

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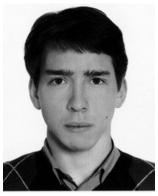

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