Disorder induced in silicon carbide by heavy-ion irradiation

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ABSTRACT

The decrease of crystal phonon peak intensities in Raman spectra of silicon carbide after heavy-ion irradiation is analyzed in relation to band-gap shrinkage and Urbach edge increase arising from accumulation of lattice disorder. The discrepancy on amorphous fractions deduced from Raman spectroscopy and Rutherford backscattering-channeling spectroscopy is addressed by taking into account the point defect formation and amorphization by displacement damage. A new analysis of Raman data is provided on the basis of the scattered light self-absorption due to damage build-up.

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I. INTRODUCTION

Many studies have shown that amorphization (loss of long-range atomic order) of silicon carbide (SiC) is resulting from accumulation of point defects (Frenkel pairs and anti-site defects) and defect-cluster formation above a threshold irradiation dose (or fluence) upon energetic electron [*1*] or ion [*2*] irradiations. Rutherford backscattering spectrometry and channeling (RBS/C) data have actually shown that complete amorphization of SiC is achieved in two steps in agreement with Molecular Dynamics (MD) simulations [*3*]: a first step corresponds to defect accumulation (to reach amorphization) and a second one of amorphous domain overlap [*4-6*]. No direct amorphization is achieved by a single ion impact in SiC. The progressive loss of long-range order is also seen by the vanishing of the narrow Raman peaks associated to phonon modes of a given polytype [*7-8*]. This corresponds to an increase of the backscattering yield in RBS/C experiments, corresponding to disorder in the Si sublattice [*7-9*].

Raman spectra of the amorphous phase (a-SiC) show the growth of broad side bands assigned to Si-Si and C-C bonds, but also distorted/disordered Si-C vibration modes, which do not exist in the parent crystalline phase [7, 8, *10, 11*]. This means that a chemical disorder has been created upon amorphization, in agreement with EXAFS data [*11*]. The short-range chemical disorder (given by the growth of the broad side bands) was correlated to the long-range disorder (given by the vanishing of narrow phonon peaks) along a three-stage process [*7-8*]. The stage I of defect accumulation in this process is consistent with the above-mentioned first step of point-defect accumulation seen by RBS/C spectrometry. However, a clear deviation was seen between these two sets of data [*6*], as found for 50-keV Ga ion irradiation of 6H-SiC in the same fluence range [*12*]. Raman spectroscopy is apparently more sensitive to low damage than RBS/C: it gives a larger disordered fraction than RBS/C in the first stage. Our aim in the present paper is to address this deviation between Raman spectroscopy data and RBS/C spectrometry data in ion-irradiated hexagonal silicon carbide.

The Relative Raman intensity (RRI) variation was used to follow the irradiation damage in SiC [*7, 8, 13*]. This RRI index is based on the decrease of the Raman peak intensities which is directly connected to the increase of the optical absorption. It reflects the long-range disorder into the crystal, even though there is no straightforward relationship between the RRI index and the lattice disorder fraction. The total disorder ($1 - A_{norm}$) was deduced from the total area A under the principal first-order Raman lines normalized to the value A_{cryst} of the crystalline material ($A_{norm} = A/A_{cryst}$) [*7, 8, 12, 13*].

Fist-order Raman peaks for frequencies between 750 cm^{-1} and 1000 cm^{-1} correspond to the transverse (TO) and longitudinal (LO) optical phonons at the first Brillouin zone (BZ) center (Γ point) for a zero momentum transfer (q = 0) [*14*]. Actually, the classical selection rules of periodic solids using the lattice-vibration wave vector are broken in a disordered solid [*15-17*]. Therefore, the folded phonon density-of-states (DOS) at the Γ point involves contributions of vibration modes of various symmetry labels from other points of the BZ [*15*]. In principle, it is challenging to monitor the decrease of long-range order by the decrease in intensity of a specific phonon peak owing to the overlap of these contributions for the same phonon energies (i.e. same Raman shifts).

The main concern is the discrepancy between the two techniques: what makes Raman spectroscopy more sensitive than RBS/C in the first step of damage? In this respect, it is known that point defects induce localized electronic levels (in stage I), and long-range disorder generates band tails of

electronic extended states in the band gap (in stage II) [*18*]. This, in turn, may induce an increase of self-absorption of Raman lines (for a laser line at photon energy E ~2.3 eV). Indeed, we have brought evidence from UV-visible absorption spectra of a clear shrinkage of the optical gap energy (E_G) from ~3 eV to 0.5 eV, and increase of the Urbach energy (E_U), with the irradiation dose, until saturation is reached for the amorphous phase [*7, 8, 19*]. Such large band-gap shrinkage is attributed to the strong disorder with homonuclear Si-Si and C-C "wrong bonds" induced in the amorphous phase. Henceforth, self-absorption of the scattered light inside the damaged layer must be taken into account.

II. DISCUSSION

Let us consider, first of all, the intensity of emitted scattered light (I_s) measured from the probed sample depth (d), and denote as α the absorption coefficient for the photon energy ($\hbar\omega$ = E) of the excitation laser light. For an attenuation of the scattered light by ~60%, we have $d \sim 1/\alpha$. The probed thickness will decrease with E_G, since in the absorption edge region for indirect gap absorption in the case of SiC, α writes:

$$\alpha = \alpha_0 \exp\left(\frac{E_G - \hbar\omega}{E_U}\right) \qquad (1)$$

where α_0 is a constant [*20, 21*]. For a-SiC, we have α ~80,000 cm^{-1} at the wavelength of 500 nm (E ~2.5 eV) [*7, 8*], that gives a probed depth of d ~0.1 µm.

Due to self-absorption, the recorded scattered intensity (I_s) for any phonon peak depends on the absorbance for a given probed depth. Assuming a flat damage profile, with constant scattered intensity ($I_{s,0}$) versus depth, the absorbance ($\mathbb{A}$) of the Raman signal writes:

$$\mathbb{A} = -\log\left(\frac{I_S}{I_{s,0}}\right) = \mathbb{A}_0 + k \exp\left(\frac{E_G - \hbar\omega}{E_U}\right) \qquad (2)$$

where $\mathbb{A}_0$ is a constant absorbance background value, and k is the Urbach parameter near 1. We define $I_{s,0}$ as the total emitted scattered intensity which is considered to be constant over sample depth. The depth dependence of the Raman signal on the damage profile is not taken into account. For a given Raman intensity ($I_{s,0}$), the absorbance ($\mathbb{A}$) will depend on E_G and E_U.

We assume that the Raman scattering cross section is not modified by resonance effects for this photon energy (E). Actually, surface Raman enhanced scattering seems unlikely for such undoped wide band-gap semiconductor at room temperature. At least, the incident photon energy must coincide with a specific defect or impurity level in the band gap, such as for doped semiconductors. However, no abrupt increase in phonon peak intensity was recorded with decreasing band gap for increasing fluence.

The next step is to correlate the optical gap shrinkage with disorder accumulation, as a function of fluence. Actually, E_G decreases versus fluence (φ) according to a second-order kinetics process:

$$E_G = E_{G,0}(1 + \sigma\varphi)e^{-\sigma\varphi} + E_{G,\infty} \qquad (3)$$

where $E_{G,0}$ = 3 eV is the band-gap energy value prior to irradiation, σ = 3.2x10^{-14} cm^2 is a damage cross section, and $E_{G,\infty}$ = 0.50 eV is the asymptotic value for a-SiC after 4.0-MeV Au ion irradiation (Fig. 1) [*7, 8, 19*]. Moreover, the Urbach energy is increasing up to an asymptotic value of $E_{U,\infty}$ = 0.56 eV versus φ with a damage cross section of σ' = 5.6x10^{-13} cm^2, with a small initial value $E_{U,0}$ close to 0 (Fig. 1):

$$E_U = E_{U,\infty}\ (1 - e^{-\sigma'\varphi}) \qquad (4)$$

By substituting Eqs. (3) and (4) in Eq. (2), one is able to calculate the relative absorbed scattered light intensity ($1 - \frac{I_S}{I_{S,0}}$) versus φ for E = 2.3 eV. Since $f_D = 1 - A/A_{cryst}$, is deduced from the integrated areas (A) of the main Raman peaks, as explained above, we use the approximation that f_D is proportional to ($1 - \frac{I_S}{I_{S,0}}$), by assuming that self-absorption is the cause of peak intensity decrease after irradiation. The decrease of Raman peak intensities is a direct evidence of the decay of the crystalline phase with ion fluence in the irradiated material consisting of the crystalline and amorphous phases. No significant broadening of the phonon crystal peaks due to disorder was found. The self-absorption of those peaks is assumed to be the same as the total scattered intensity, since the Raman shift is very small. We neglect the change in reflectance, related to refractive index variation with fluence [*22*] that would simply give an offset of the curve. The onset of stage I of damage for φ ~1x10^{12} cm^{-2} corresponds to the onset of band-gap narrowing and onset of Urbach energy saturation due to point-defect build up (Fig. 1). In stage II for $\varphi \geq$ 3x10^{13} cm^{-2}, the increase of f_D corresponds to the onset of absorption for $E \geq E_G$, and the saturation for $\varphi \geq$ 3x10^{14} cm^{-2} corresponds to the saturation of optical gap in a-SiC.

The disordered fraction can be fitted by using a trial-and-error method by varying the $\mathbb{A}_0$, k, and cross section values.The evolution of ($1 - \frac{I_S}{I_{S,0}}$) versus fluence looks similar to the evolution of disordered fraction measured by Raman spectroscopy by using two different cross sections: σ = 1.0x10^{-14} cm^2 and σ' = 2.0x10^{-13} cm^2, and the following parameters: A_0 = 0.03, k = 1.3, $E_{G,\infty}$ = 0.50 eV, and $E_{U,\infty}$ = 0.70 eV. The background absorbance ($\mathbb{A}_0$) is rather consistent with the reflectance loss (R ~20%) at the SiC/air interface deduced from Fresnel's equation and a refractive index of n = 2.66 for E = 2.3 eV. This yields a background absorbance of $\mathbb{A}_0 = -\log(0.8) \sim 0.1$ corresponding to the reflectivity of the laser light at the sample surface. The calculated value of ($1 - \frac{I_S}{I_{S,0}}$) with a scaling factor of 3.2 is shown in Fig. 1 (blue dotted curve). Even though those two cross sections deviate slightly from the least-

square fits of E_G and E_U data versus fluence, this evolution can account for the RRI procedure, as discussed above.

For comparison, the σ values deduced from RBS/C data for 6H-SiC at a 600 nm depth are of 1.84×10^{-14} cm^2 for a single impact model [*5*] and 3.0×10^{-14} cm^2 for the stage II [*4*]. Fitting the Raman data with the multi-step damage accumulation (MSDA) model yields the damage cross sections of 1.3×10^{-13} cm^2 and 1.1×10^{-14} cm^2 for stage I and stage II [*6*], respectively, that are in rather good agreement with the present σ' and σ values, respectively. However, this MSDA analysis is an *ad-hoc* modelling which does not give any physical explanation of those two cross sections. Fitting the RBS/C data at 600-m depth with the MSDA model (Fig. 1, black dotted curve) gave cross sections of 2.5×10^{-14} cm^2 and 3.0×10^{-14} cm^2 for stage I and stage II [*6*], respectively, which are clearly different from those of Raman spectroscopy data. This deviation definitely arises from the different physical processes associated to these two kinds of measurements. RBS/C spectroscopy is based on the scattering of channelled particles in the crystal rows, whereas Raman spectroscopy is based on the inelastic scattering of light by optical phonon modes. The background and saturation values of f_D (Fig. 1) are also different due to the different processes involved in those measurements.

III. CONCLUSION

In summary, the evolution of the amorphous fraction of heavy-ion irradiated SiC on the basis of the RRI of Raman spectra is accounted for by the band-gap reduction and Urbach energy increase due to disorder accumulation. The two different stages correspond to the different cross sections of those two processes. In stage I, the Urbach energy increases up to saturation when reaching stage II of the onset of amorphization. The band-gap energy starts to clearly decrease at the end of stage I due to band tailing and saturates when full amorphization is achieved.

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Fig. 1: Relative absorbed scattered light intensity (1- $\frac{I_S}{I_{S,0}}$), for a photon energy E = 2.3 eV (left scale with a scaling factor of 3.2, blue dotted curve), disordered fraction (f_D) deduced from Raman spectra (full circles) and RBS/C spectra at 600-nm depth (open circles) (left scale), and optical gap (E_G) deduced from UV-visible absorption spectra (right scale) for 4.0-MeV Au ion irradiation [*7, 8*], as a function of fluence. The solid curve is the fit of E_G values with Eq. (3). The dashed curve is the fit of E_U values with Eq. (4). The blue dotted curve is the fit of f_D Raman data using Eqs. (2)-(4). The black dotted curve is the fit of f_D RBS/C data with the MSDA model [6]. The vertical dashed line divides the first and second stages of damage. The horizontal arrows mark the values of laser excitation (E = 2.3 eV) and initial band gap value ($E_{G,0}$ = 3 eV).

