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Simulations on effects of granular morphology on single-electron and optical spectra of nano- and micro-crystalline AlN and diamond

V. Ligatchev [a,b,*], K.P. Ong [b], P. Wu [b]

[a] NanoScience Innovation Pte. Ltd., Singapore 139948
[b] Institute of High-Performance Computing, 1 Science Park Road #01-01, Singapore 117528

Abstract

In the present study, effects of geometry of the granular morphology on particularities of the $N(E)$ distributions and optical absorption spectrum in nominally undoped nano- and micro-crystalline AlN and diamond are simulated within a framework of a semi-empirical adiabatic 'Generalized Skettrup Model' (GSM). Obtained simulation results reveal, that alterations in the grain sizes mostly affect relatively deep (i.e. defect) intra-grain states, while band tail electron states are influenced pretty weakly. Amendments in a shape of the crystalline grains also cause considerable alterations in the intra-grain single-electron spectrum of the poly-crystalline layers and powders of AlN and diamond, though such effects are not as strong as the ones that originated from the grain size changes in the range from nano-meters to microns. Results of our semi-empirical simulations match well with corresponding experimental data, previously reported for single-micro- and nano-crystalline AlN and diamond, and might give physically transparent guidelines for adjustment optical and electronic properties of such materials for their various applications.

Keywords: Nano- and micro-crystalline diamond; Aluminum nitride; Acoustic and optic confined phonons; Electron and optic spectra

1. Introduction

Polycrystalline modifications of aluminum nitride (AlN) and diamond are mostly demanded for new generation of electronic devices, particle and light detectors, tool coatings and biomedical applications. Therefore, physical mechanisms, which are linking characteristics of polycrystalline morphology of these wide band gap semiconductors, and their optical, photoelectrical, electrical and mechanical parameters, are crucially important from both fundamental and application viewpoints. Profound effects of shape and sizes (i.e. geometry) of polycrystalline morphology of diamond and AlN on characteristics of confined optical phonons, photoluminescence, and optical absorption in these materials are known for more than 15 years [1–3]. Nevertheless, significant controversies still remain in experimental data, measured on the polycrystalline AlN and diamond layers and powders composed of different average grain sizes, as well as in theoretical interpretations of these experimental results. For example, the 'effective' band gap width E_G determined by the '10^4-cm^{-1}' criterion for ozone-cleaned ultradisperse diamond (UDD) with average grain sizes of ~ 4 nm is 3.5 eV [4]; i.e. E_G of the UDD is *lower* than the corresponding parameter of the bulk diamond (5.45 eV [5]). These thin UDD layers were precipitated from a water suspension. On the other hand, both effective medium approximation (EMA) [6] and density functional theory (DFT) [7] predict *larger* optical gap of the nano-diamond compared to that of the bulk (single-crystalline) material when the grain sizes are less than 2 nm. Results of optical measurements, published in Ref. [8] (see Fig. 3 therein for details), reveal a successive decrement in E_G for freestanding nano-, sub-micro- and micro-crystalline diamond films (average grain sizes are of 20, 400 and 600 nm, respectively). Diamond films, studied in that article, have been prepared by microwave CVD (MW CVD) technique, using nitrogen–methane–hydrogen mixtures; thus, considerable contamination of the films with nitrogen might happen. Nevertheless, in Ref. [8], observed effect of the diamond morphology on optical properties of the material has been mainly attributed to a substantial reduction in surface roughness of the layers, containing grains with smaller

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* Corresponding author. NanoScience Innovation Pte. Ltd., Singapore 139948. Tel.: +65 64191326 (Office), +65 91870780 (Mobile).
E-mail address: ligatchev@hotmail.com (V. Ligatchev).

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average sizes, while possible influence of the incorporated nitrogen on the optical properties of studied layers has been ignored completely. Optical absorption of oxygen-contaminated single-crystalline AlN films grown epitaxially on sapphire substrates have been studied in the photon energy ($h\nu$) range from 3.5 to 6.5 eV elsewhere in Ref. [9]. Surface morphology of those films comprises of hexagonal pyramids and triangular crack patterns, probably caused by a large mismatch in lattices spacing of the sapphire and AlN. It was found, that a sub-gap optical absorption (observed at $3.5 \leq h\nu \leq 5.0$ eV) rises considerably and monotonically when the AlN film thickness increases from 4 to 9 μm [9], though no comments on a possible physical nature of this enlargement have been given in the article. Room-temperature E_G and E_U energies (the latter one stands for a characteristic energy of the Urbach tail slope[1], which is derived from an exponential tail in a spectral dependence $\alpha(h\nu)$ of the optical absorption coefficient) of AlN are also found to be affected considerably by the parameters of the crystalline morphology: $E_G \cong 6.2$ eV and $E_U \cong 90$ meV have been reported for ~500 nm thick single-crystalline AlN films grown epitaxially on <0001> oriented sapphire substrates [10], while $E_G \cong 4.8$ eV (determined by the '10^4-cm^{-1}' criterion) and $E_U \cong 674$ meV where estimated for the nano-crystalline AlN films with average grain size of 20 nm [2]. All above-mentioned variations in optical properties of nano-crystalline diamond might originate from changes in a distribution $N(E)$ of a single-electron density of states both within and just beyond the bandgap of these materials. An example, illustrating a character of interrelations between $N(E)$ and $\alpha(h\nu)$ spectra in nano-crystalline diamond is given in Ref. [11]. In that paper, an increment in both sub-gap and band-tail optical absorptions of nitrogen-doped MW CVD nano-diamond samples (compared to nominally undoped ones) has been detected using photo-thermal deflection spectroscopy and spectrally resolved photoconductivity techniques. Observed augmentations in the optical absorptions coefficient have been attributed to a broadening of $N(E)$ peaks related to π- and π^*-bonds, as well as to a considerable increment in the density of states in the conduction band tail of the nitrogen-doped samples [11]. In the present study, we simulate influences of a geometry of the granular nano- and micro-morphology on parameters of the $N(E)$ and $\alpha(h\nu)$ spectra of nominally undoped AlN and diamond layers and powders within a framework of a semi-empirical adiabatic 'Generalized Skettrup Model' (GSM), described in the second section. It allows us to clarify effects of the morphology on the electron and optical spectra in the intrinsic polycrystalline wide band gap semiconductors with both pure covalent and partially ionic character of chemical bonds (see third section of this paper), and separate these effects from other possible mechanisms (like impacts of grain boundaries, dopands, etc.) of modification of the optical properties of these materials.

2. Simulation technique and parameters

The GSM was proposed in Refs. [12–14], and has been previously employed at simulations the $N(E)$ and $\alpha(h\nu)$ spectra both in amorphous hydrogenated silicon (a-Si:H) films [13,14] and polycrystalline layers of MW CVD diamond [15]. This model is essentially based on the Tauc's approximation of the 'virtual crystal', created for theoretical investigations of optical properties of non-crystalline semiconductors [16]. Abe and Toyozawa employed this approximation for $N(E)$ simulations in such materials [17], and disorders could be correlated (according to Gaussian law), uncorrelated or anti-correlated between the valence band (VB) and conduction band (CB) states [18]. Within a framework of GSM, thermally-induced structural disorders in semiconductors with purely covalent inter-atomic bonds are formally represented by statistical characteristics of multiple confined *acoustic* vibrations (phonons), which could interact with both the bonding VB electron states and anti-bonding CB ones [14,15]. Spatial extents (volumes) of the phonon confinement were presumed to be equal to average sizes of polycrystalline grains in the CVD diamond [14] or amorphous columns in spatially non-homogeneous structure of columnar a-Si and a-Si:H films [14]. An existence of optic phonons has been totally ignored in the previous version of the GSM [14,15]. This simplification seems to be fairly reasonable for pure covalent structure of sp^3-hybridized atomic network within the diamond grains, but definitely does not match well for AlN materials with a significant (about of 0.43–0.45 [19]) ionic component of the inter-atomic potential. Therefore, different modifications of the GSM are used herein for simulation spectroscopic characteristics of polycrystalline diamond and AlN. Principal equations of the first modification (which ignores all effects associated with the bond ionicity and optic phonons) are exactly the same as those in Ref. [15]:

$$N_{\mathrm{c}}(E) = \frac{ZD}{B_{\mathrm{c}}} W_{\mathrm{c}}^{\mathrm{a}}[E_{\mathrm{G}}(0) - E], \tag{1a}$$

$$N_{\mathrm{v}}(E) = \frac{ZD}{B_{\mathrm{v}}} W_{\mathrm{v}}^{\mathrm{a}}(E). \tag{1b}$$

$$W_{\mathrm{c,v}}^{\mathrm{a}}(E) \cong \exp\left(-\frac{E}{k_B T B_{\mathrm{c,v}}}\right) \int_{\mathrm{M0}}^{\infty} \frac{1}{Z_{\mathrm{M}}[\Gamma(M)]^{r1}} \left[\frac{2L_x L_y F(L_x, L_y, L_z) E^2}{M^{r2} (B_{\mathrm{c,v}} h c_{\mathrm{s}})^2}\right]^M \mathrm{d}M, \tag{2}$$

where D is an average atomic density, Z is the atomic valency, B_{v} and B_{c} are dimensionless constants which characterize the intensity of interactions of the confined longitudinal acoustic phonons with charge carriers on bonding (within VB) and anti-bonding (within CB) electron levels, respectively; ZQE/B is an instant value of an aggregate energy of *all* longitudinal acoustic phonons, confined at the given moment in time in a rectangular coherency cell with orthogonal edges of the lengths L_x, L_y, L_z; Q is the number of atoms (of a single sort) in the confinement volume ($Q \equiv D * L_x * L_y * L_z$), $M = N/ZQ$ and $M0 = N0/ZQ$, $N0$ is the integer

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[1] Although Urbach energy nowadays is used most frequently for characterization amorphous semiconductors and insulators, it is worth to remind that the exponential (Urbach) tail in the spectral behavior of the optical absorption coefficient was originally discovered for *crystalline* AgBr (see Fig. 2 in: F. Urbach, *Phys. Rev.* **92** (1953) 1324).