

Electronic structure of silicon carbide containing superstoichiometric carbon

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Electronic structure of superstoichiometric silicon carbide, $\beta\text{-SiC}_{x>1.0}$, was studied by the self-consistent *ab initio* linearized "muffin-tin" orbital method. It is most likely that the formation of $\beta\text{-SiC}_{x>1.0}$ occurs by replacement of silicon atoms by carbon atoms rather than by insertion of carbon atoms into interstitial lattice sites. The $\text{C} \rightarrow \text{Si}$ replacement is accompanied by lattice compression (the equilibrium lattice parameter for a superstoichiometric phase of composition $\text{Si}_{0.75}\text{C}_{1.25}$ is ~2% smaller than for SiC). In the presence of superstoichiometric carbon the type of interaction between silicon and carbon atoms changes and additional bonds characteristic of diamond are formed.

Key words: silicon carbide; superstoichiometric carbon; electronic structure; chemical bond.

Silicon carbide synthesized by traditional methods is a stoichiometric compound^{1,2} under equilibrium conditions (according to Ref. 3, the deviation from the stoichiometric composition of SiC does not exceed 10^{-5} % at.).

Previously,⁴ the possibility of obtaining $\beta\text{-SiC}$ containing superstoichiometric carbon, which is a non-equilibrium product of the $\text{Si} + \text{C} \rightarrow \text{SiC}$ reaction, has been reported. Exfoliated graphite⁵ was used as an active carbon component. The results of X-ray phase analysis of the product synthesized from exfoliated graphite and Si suggested that a supersaturated solid solution (SS) of carbon in $\beta\text{-SiC}$ was obtained. A line corresponding to diamond (111) phase was observed on the X-ray photograph of a virtually single-phase $\beta\text{-SiC}_{x>1.0}$ polycrystal subjected to heat and pressure treatment. The content of diamond (111) phase in the specimen was 5 to 8%.⁴ It is assumed that sintering of highly disperse $\beta\text{-SiC}_{x>1.0}$ powders can favor production of nanocrystalline ceramics in the SiC –diamond system.

In this work we studied the mechanism of formation of superstoichiometric $\beta\text{-SiC}_{x>1.0}$ and its electronic structure.

A unit cell of silicon carbide that crystallizes according to the sphalerite type contains four SiC structural units. Atoms of one element (e.g., Si) occupy sites of a face-centered cubic cell. Atoms of the second element (C) occupy the centers of four of the eight small cubes. Empty octants alternate with occupied octants along all three coordinate directions. Both atomic positions are equivalent.

Electronic structure of stoichiometric and superstoichiometric silicon carbide was calculated by the self-consistent *ab initio* linearized "muffin-tin" orbital method (LMTO).⁶ Closest packing of the structure was achieved by introducing two types of hollow spheres, E_{Si} and E_{C} , with radii equal to those of "muffin-tin" orbitals of

corresponding atoms. Three possible mechanisms of the formation of superstoichiometric silicon carbide were considered: (1) filling of E_{Si} interstitial lattice sites with carbon atoms, (2) filling of E_{C} interstitial lattice sites with carbon atoms, and (3) replacement of silicon atoms in regular positions by carbon atoms. The probability for each type of insertion of an extra C atom to occur was evaluated from the difference in the cohesive energies (ΔE) of stoichiometric and superstoichiometric crystals calculated as differences between the total energy of the corresponding system and that of free atoms constituting the system.

The calculated ΔE values for mechanisms 1 and 2 were 0.24 and 0.35 Ry, respectively, which makes the formation of superstoichiometric carbide by carbon insertion into interstitial lattice sites unlikely. For the third mechanism ($\text{C} \rightarrow \text{Si}$ replacement) the ΔE value decreases by an order of magnitude but remains positive ($\Delta E = 0.03$ Ry.) The obtained ΔE value is small even at the high concentration of superstoichiometric carbon (25%) used in the calculations. Under actual conditions of synthesis (high pressure and temperature, and low concentration of superstoichiometric carbon) the replacement energy can take negative values, thus making mechanism 3 energetically possible.

Then we studied the dependence of the total energies of systems (E_{total}) on the lattice parameter, which simulated the effect of external hydrostatic pressure. From Fig. 1 it follows that for superstoichiometric carbide the lattice parameter is ~2% smaller than for the initial $\beta\text{-SiC}$. It should be noted that a decrease in the lattice parameter (by 0.16%) was detected experimentally for a supersaturated solution of C in SiC .⁴

The ΔE value calculated for the equilibrium lattice parameter of $\beta\text{-SiC}_{x>1.0}$ remains positive; however, it

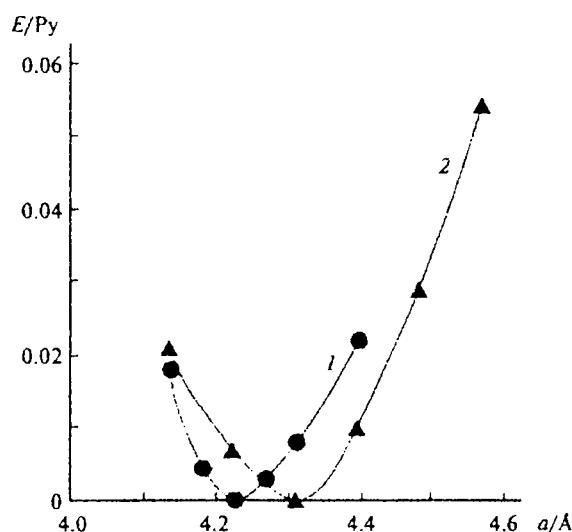


Fig. 1. Dependence of the total energy on the lattice parameter a for superstoichiometric silicon carbide of composition $\text{Si}_{0.75}\text{C}_{1.25}$ (1) and stoichiometric β -SiC silicon carbide (2); calculations by the LMTO method. The curves 1 and 2 are referred to the point $E_{\min} = 0$.

decreases to a value of 0.02 Ry. Further calculations showed that the ΔE value changes its sign and takes a value of -0.01 Ry upon local compression (by 10%) of the nearest environment of C(1) carbon atoms that replace silicon atoms in the β - $\text{SiC}_{x>1.0}$ structure. Such a local crystal lattice relaxation in the vicinity of impurity atoms should occur since the carbon atom has a smaller covalent radius than the silicon atom.

Let us compare the total and partial densities of states (DOS) for stoichiometric and superstoichiometric silicon carbide (Figs. 2 and 3, respectively).

The electron energy spectrum of SiC calculated in this work consists of two valence bands separated by a band gap, which is in good agreement with previous calculations and with the data of X-ray emission and electronic spectroscopy.⁷⁻⁹ The C 2s and Si 3s states make major contributions to the low-energy band I, while the C 2p and Si 3s,3p states make the major contributions to the upper band II. For the carbon atom, p-orbitals make virtually no contribution to band I and s-states make a small contribution to band II, which indicates an insignificant role of s-p-hybridization. The role of s-p-hybridization for the silicon atom is more important. The contribution

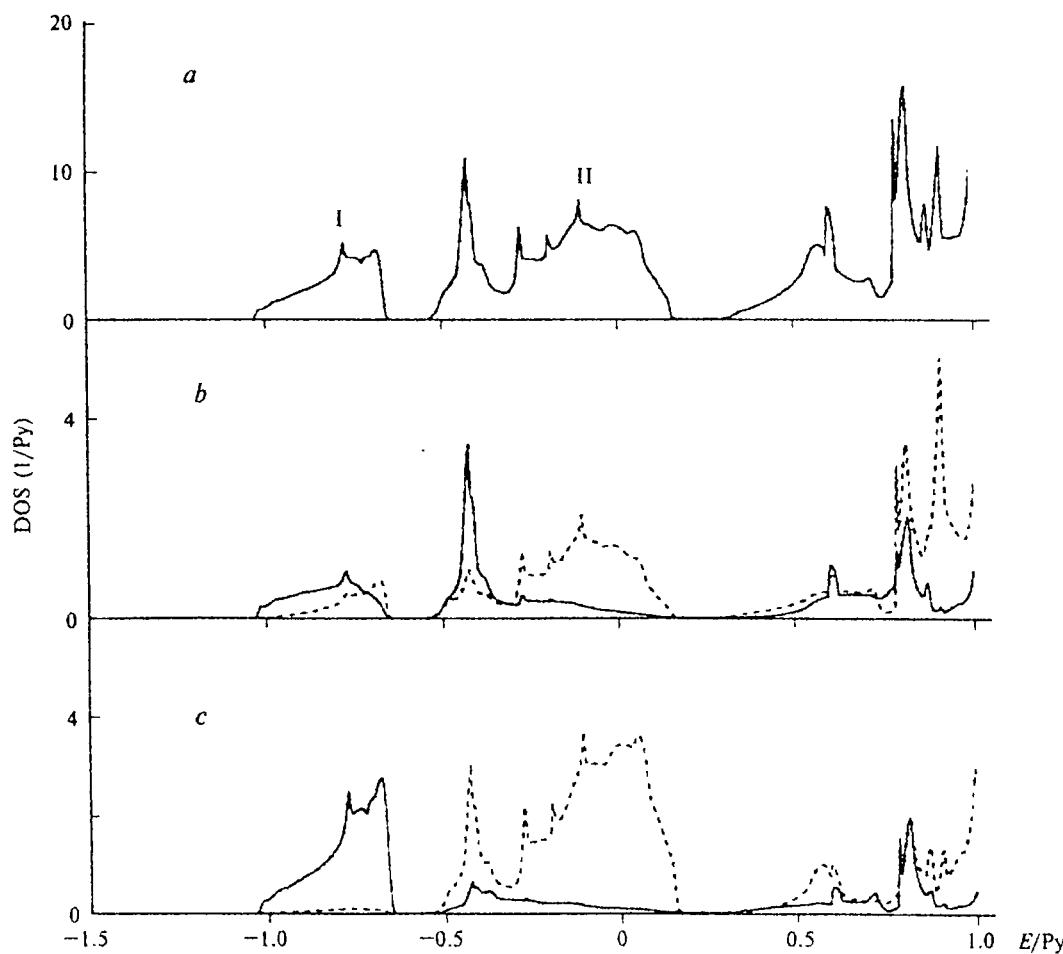


Fig. 2. Total (a) and partial (b, c) densities of states for Si (b) and C (c) atoms of stoichiometric silicon carbide. The distributions of Si 3s and C 2s states are shown by a solid line and those of Si 3p and C 2p states are shown by a dashed line.

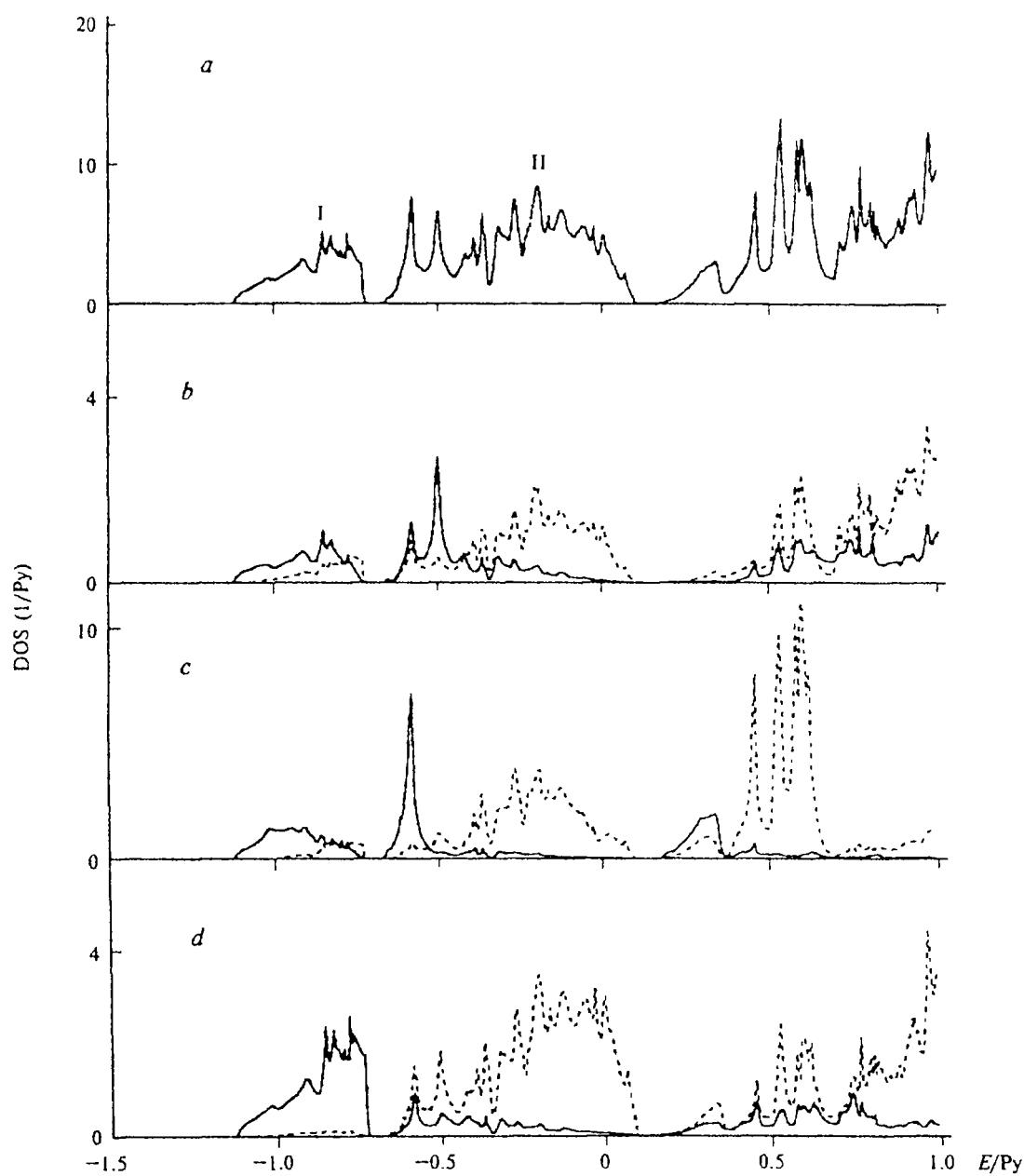


Fig. 3. Total (a) and partial (b-d) densities of states for superstoichiometric silicon carbide with optimized lattice parameter a for Si (b), C(1) (c), and C (d) atoms. The DOS for the C(1) carbon atom, which replaces a silicon atom in the β -SiC unit cell, are highlighted. The distributions of Si 3s and C 2s states are shown by a solid line and those of Si 3p and C 2p states are shown by a dashed line.

of Si 3p orbitals to band I is rather large, while the low-energy peak of band II is composed mainly of Si 3s states. The high-energy region of this band is composed of p states of silicon and carbon only.

The structure of band I and, especially, that of band II in the spectrum of superstoichiometric silicon carbide is more complex (Fig. 3). The most pronounced distinctions are observed for the DOS of nonequivalent carbon atoms. Characteristic of superstoichiometric carbon atom

C(1) is an increase in the s-p-hybridization, which leads to an increase in the contribution of p states to band I and to the appearance of a large peak of 2s states in the low-energy region of band II, which is responsible for a bimodal structure of the TDOS of this valence band.

The calculated partial charges of the "muffin-tin" sphere indicate that nonequivalent carbon atoms play different roles in chemical bonding. The charge state of silicon atoms for the β -SiC and β -SiC_{x>1.0} phases changes

insignificantly. An s-p charge transfer is observed for the C(1) carbon atom, which is a central atom in the [C(1)C₄] "microcluster" in the bulk of the superstoichiometric phase.

According to calculations, the charges of the "muffin-tin" sphere of the C(1) atom are 1.35 (C 2s state) and 2.34 e (C 2p state), which indicates that new sp³-like carbon-carbon bonds similar to interatomic bonds in diamond lattice are formed in the bulk of carbon microclusters in β -SiC_{x>1.0}.

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Synthesis of 3-nitro-3-azalk-2-yl ethers

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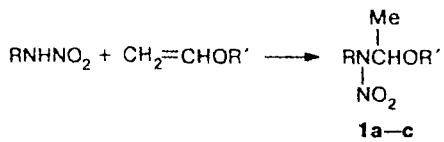
Primary *N*-nitramines react with vinyl ethers to give 3-nitro-3-azalk-2-yl ethers.

Key words: primary *N*-nitramines, vinyl ethers, 3-nitro-3-azalk-2-yl ethers.

Polar addition of compounds bearing a reactive hydrogen atom to the double bond of vinyl ethers is well known,^{1,2} whereas literature data on the reaction of the latter with primary *N*-nitramines are lacking.

We established that this reaction occurs in the presence of a mineral acid (H₃PO₄ or H₂SO₄) as a catalyst to give 3-nitro-3-azalk-2-yl ethers (**1a-c**), which were not found in the literature³⁻⁵ to be synthesized in the common ways.

Primary *N*-nitramines react with *n*-butyl vinyl ether even at 30–35 °C to give products **1a** and **1c** in 52.3% and 30.5% yields, respectively. The reaction with vinyl



R = Me, R' = Bu (**a**); C₂H₅Cl (**b**); R = Et, R' = Bu (**c**)

ethers containing an electron-accepting substituent requires heating (60 °C), which decreases the yield of **1b** to 24.5% (converted to vinyl ether) owing to stimulation