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Theoretical Study of Atomic Structure of Solid Solution $Al_{1-x}Sc_xN$

Svetlana A. Bondarenko[*]
Technological Institute for Superhard and Novel Carbon Materials
Tsentral'naya, 7a, Troitsk, Moscow, 142190
Moscow Institute of Physics and Technology
Institutskiy per., 9, Dolgoprudny, Moscow Region, 141701
Russia

Boris P. Sorokin
Pavel B. Sorokin
Technological Institute for Superhard and Novel Carbon Materials
Tsentral'naya, 7a, Troitsk, Moscow, 142190
Russia

The features of atomic structure of $Al_{1-x}Sc_xN$ in the whole Sc concentration were studied using ab initio DFT approach. The possible segregation of AlN and ScN phases in a solid solution was investigated and results were compared with available reference data. Close agreement between theoretical models and experimental structures of phases investigated has been pointed out.

Introduction

Aluminum nitride (AlN) is a piezoelectric material with a high phase velocity of longitudinal acoustic wave (11000 m/s), high thermal conductivity, high temperature and chemical resistance. Currently it is considered as one of the most attractive piezoelectric materials for use in acoustoelectronic devices [1].

Aluminum nitride can exist as the wurtzite or sphalerite structures. Hexagonal aluminum nitride is interesting due to good piezoelectric properties. High thermal conductivity makes aluminum nitride a suitable material to prevent plate heating in silicon technology in the manufacture of microelectronic circuits. On the other hand scandium nitride (ScN) is a cubic crystal, with the space symmetry group $Fm3m$ and the rock salt structure, which leads to the absence of piezoelectric properties. However, available experimental data suggests the significant increase of the piezoelectric constant (more than in four time) in a solid solution $Al_{1-x}Sc_xN$ with an increase a scandium concentration [2]. Coexistence of two phases is observed in the solid solution structure: hexagonal piezoelectric type of AlN wurtzite (wz) and ScN centrosymmetrical cubic one (rs).

Understanding of a nature of the piezoelectric, elastic, and other physical properties of the $Al_{1-x}Sc_xN$ solid solution requires detailed information about its structure. At the moment, the simulation of the $Al_{1-x}Sc_xN$ atomic geometry was carried out only within the framework of the quasirandom structure method [3, 4] or the gradual substitution of Al atoms by Sc atoms in the wurtzite $Al_{1-x}Sc_xN$ structure [4], which, however, does not directly related to experimental data on the segregation of AlN and ScN phases in a solid solution. The work presented is devoted to

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[*]svetlana.bondarenko@phystech.edu

the span this gap and provide the experimentally related investigation of the atomic structure of $Al_{1-x}Sc_xN$.

Computational method

Quantum-chemical simulation was performed within the framework of density functional theory (DFT) [5, 6] using plane-wave basis set and the PAW method [7, 8] as implemented in VASP [9–11]. Generalized gradient approximation (GGA) was used in the form of PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional [12]. For the Brillouin zone sampling gamma-centered Monkhorst-Pack scheme [13] with the $6 \times 6 \times 2$ k-point mesh (for the smallest unit cell) was chosen. The plane wave basis cut-off energy $E_{cutoff} = 350$ eV was used. In all geometry optimizations the convergence criterion was required as the maximal force acting on any atom was less than 0.01 eV/Å.

The aluminum nitride and scandium nitride unit cells in the wurtzite and rocksalt phases respectively were relaxed and they lattice parameters were obtained. The unit cell of aluminum nitride contained 4 atoms (two atoms of aluminum and two nitrogen atoms) had lattice parameters $a = b = 3.253$ Å and $c = 5.213$ Å, which are in good agreement with the experimental data $a = b = 3.112$ Å and $c = 4.982$ Å [14]. The unit cell of scandium nitride consisted of 8 atoms (4 scandium atoms and 4 nitrogen atoms), in which the following lattice parameters were obtained as: $a = b = c = 4.500$ Å. This result also agrees well with experiment [15]: $a = b = c = 4.450$ Å.

Results and discussion

The simulation of the atomic structure of the solid solution $Al_{1-x}Sc_xN$ with different scandium concentration was carried out. Since chosen method of theoretical investigation takes into account periodic boundary conditions and does not allow the direct simulation the solid solution structure therefore two types of structures were studied. The first type is the wz-AlN (Fig. 1a) and rs-ScN (Fig. 1b) supercells. The atoms in both supercells were uniformly substituted by Sc and Al atoms, respectively. The second type was considered as a supercell containing both the wz-AlN and rs-ScN phases in accordance with the experimental results of the coexistence of two phases [2] (Fig. 1c). Such a structure can be realized because from the symmetry point of view, the 6th-fold axis in the wurtzite along the [001] direction is compatible with the third-fold axis in the rock salt structure coinciding the [111] direction. Such combined phase presents a combination of the wz-AlN and rs-ScN films via the (001) and (111) surfaces junction. Interatomic distances in these planes are close to each other (3.253 and 3.182 Å, the discrepancy about 2.2 %) which allows us to conclude that the epitaxial conditions have been realized, and the structures of both phases are slightly distorted after relaxation and only negligibly impact on the final result.

In the $Al_{1-x}Sc_xN$ solid solution within a whole concentration range ($0 < x < 1$), the atomic geometries of both types of supercells have been optimized and its average binding energy per atom has been calculated. Despite the fact that in general it is not correct to compare the average energies of a system of solid solutions with different numbers of atoms of different types, it is possible to compare the energies of structures with the same stoichiometry. This makes possible to estimate the energy favorable structures of a solid solution with a chosen concentration ratio Sc:Al, and thus to find which phase should be realized really. The obtained results are presented in Fig. 2. The first type of $Al_{1-x}Sc_xN$ solid solution (wz-AlN and rs-ScN supercells with substituted Sc and Al atoms, respectively) is presented by a line with circles and triangles, respectively, and second type containing both wz-AlN and rs-ScN (Fig. 1c) is shown by the rhomb line.
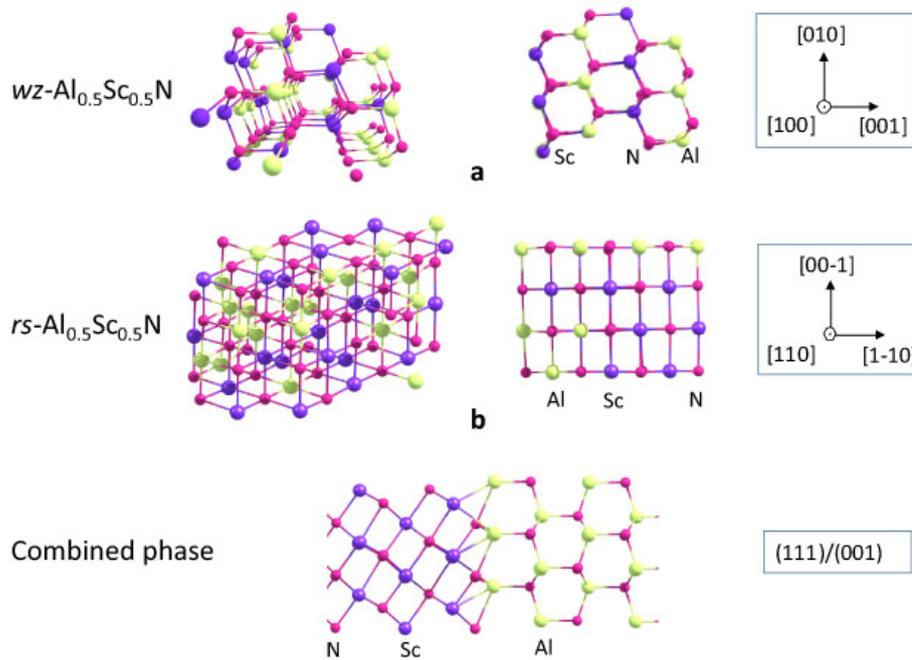
Fig. 1. Hypothetical atomic models of the $Al_{1-x}Sc_xN$ solid solution for $x = 0.5$ a) $Al_{0.5}Sc_{0.5}N$ in the wurtzite phase (the (001) and (100) projections are shown); b) $Al_{0.5}Sc_{0.5}N$ in the rock salt phase (a general rs structure view and the (110) projection are shown); c) combined structure of $Al_{0.5}Sc_{0.5}N$ contained both phases as wz-AlN and rs-ScN
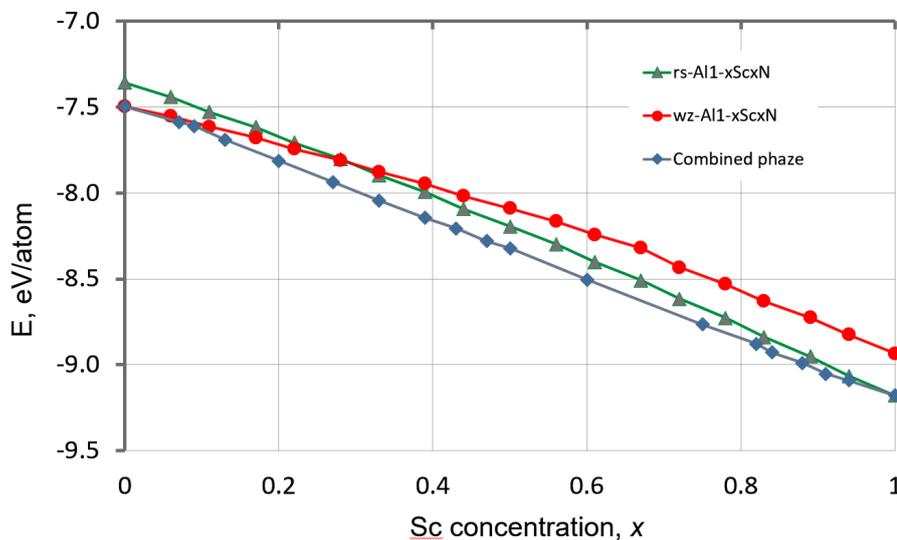

Fig. 2. Dependence of the energy per atom for two types of structures of solid solutions $Al_{1-x}Sc_xN$ as a function of scandium concentration x. Energy of structures of first type are marked by circles (wz-$Al_{1-x}Sc_xN$) and triangles (rs-$Al_{1-x}Sc_xN$), whereas energy of combined phase is marked by diamonds

It was found that comparison of the energies for the first type structures, at $0 < x < 0.34$, the wurtzite phase has a lower energy. At the $x = 0.34$, the energy dependences for wz-AlN and rs-ScN cross which indicates the transformation from the wurtzite to the rock salt phase. At a higher concentration, the rock salt phase rs-Al$_{1-x}$Sc$_x$N becomes favorable by the lower energy. On the other hand, taking into account the structures of the second type the physical picture of the phase transformation could be explained more clearly. Indeed, the transition from the pure wurtzite phase wz-Al$_{1-x}$Sc$_x$N to the phase containing both wurtzite AlN and rock salt ScN phases is observed within any non-zero Sc concentration. The fraction of rs-ScN phase monotonically increases with increasing of the scandium content which is represented by the lower energy of the combined phase than the energy of the phases (both wz-AlN and rs-ScN) in the whole Sc concentration range. This means that within the approximation used the most stable structure will be that both phases are coexisted together. This corresponds well with TEM images confirming the presence of both phases in solid solution [2].

Conclusion

The dependence of the energy of the Al$_{1-x}$Sc$_x$N structure on the scandium concentration x was investigated. It was found that aluminum-scandium nitride solid solution at any scandium concentration tends to transform into a phase contained both the AlN wurtzite phase and the ScN rock salt phase. With increasing of the scandium concentration, the rs-ScN part increases monotonically up to perfect rs-ScN structure. This indicates that within the framework of a chosen approximation the most stable structure should contain two segregated phases, in accordance with the experimental data. The domain of existence of the predominantly wurtzite phase is most interesting from the point of view by the presence of piezoelectricity, and the theoretical model of the piezoelectric effect should be done in further study.

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Теоретическое исследование атомной структуры твердого раствора $Al_{1-x}Sc_xN$

Светлана А. Бондаренко

Технологический институт сверхтвердых и новых углеродных материалов
Центральная, 7а, Троицк, Москва, 142190
Московский физико-технический институт
Институтский пер., 9, Долгопрудный, Московская обл., 141701
Россия

Борис П. Сорокин
Павел Б. Сорокин

Технологический институт сверхтвердых и новых углеродных материалов
Центральная, 7а, Троицк, Москва, 142190
Россия

Изучены трансформация и особенности кристаллической структуры $Al_{1-x}Sc_xN$ во всей области концентраций Sc с использованием ab initio DFT метода. Исследована возможная сегрегация фаз AlN и ScN в твердом растворе, проведено сравнение с имеющимися экспериментальными данными. Отмечено близкое согласие теоретических моделей и экспериментальных структур исследованных фаз.

Ключевые слова: твердый раствор, фазовая трансформация, DFT.