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2001 J. Phys.: Condens. Matter 13 8881

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High-nitrogen-pressure growth of GaN single crystals: doping and physical properties

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Received 2 May 2001

Published 20 September 2001

Online at stacks.iop.org/JPhysCM/13/8881

Abstract

Growth of GaN under high-pressure high-temperature conditions allows one to obtain large-size high-quality GaN single crystals. These crystals have high concentration of free electrons, most likely due to a high concentration of O impurity replacing nitrogen in the N sublattice. The incorporation of oxygen impurity during high-pressure growth of GaN single crystals was investigated using quantum mechanical density functional theory calculations. It was shown that the adsorption of oxygen in liquid group III metals (Al, Ga and In) leads to dissociation of the O₂ molecule. The dissociation process proceeds without energy barrier.

The transition of oxygen from the adsorbed position into the interior of the Al has been also investigated. The results of calculations indicate that the direct transition energy barrier is about 3 eV. This indicates that the dissolution of oxygen into liquid group III metals proceeds via Brownian motion of O-containing clusters. This also explains the difference between the solid and liquid surfaces: the solid surfaces undergo passivation by oxygen, whereas in the liquid metal the oxygen is dissolved.

The doping of Mg during growth leads to a change of the electric properties of GaN crystals—they become highly resistive. Mg doping changes the morphology of the plate-like GaN crystals. The physical properties of GaN:Mg crystals will be reviewed and compared with undoped GaN crystals.

Beryllium doping is considered as an alternative route to obtaining p-type GaN. The doping with Be during growth increases the resistivity of the Be-doped GaN. However, the optical properties of Be-doped GaN crystals are different. These properties will be compared with Mg-doped and undoped GaN crystals.

1. Introduction

The effective doping of GaN and its solid solutions with AlN and InN plays a crucial role in the application of nitride semiconductors to electronic and optoelectronic devices. Nitride semiconductors are characterized by relatively low mobility of p-type carriers [1]. Also, the typical concentration of holes is rather low in all of the p-type layers obtained [2]. At present, the low conductivity of p-type materials is one of the limiting factors in the technology of nitride devices. Therefore, investigation of the doping of group III nitrides is very important for basic research and applications.

Magnesium is the principal acceptor impurity that is commonly used in most of present day p-type group III nitrides. Doping with Mg in MOCVD processes, in presence of the NH_3 , leads to creation of Mg–H complexes, which behave as donors [3]. This lowers the energy of the complex, allowing the introduction of more Mg during growth of the layers. Afterwards, Mg can be activated by annealing in a hydrogen-free atmosphere, using temperatures close to 800 °C [4]. Nevertheless, due to the comparatively high energy of the acceptor, close to 150 meV, the concentration of holes in the valence band is quite low at room temperature.

High-nitrogen-pressure growth of GaN allows one to obtain high-quality single crystals of a linear size close to 20 mm [5, 6]. In processes where pure liquid Ga is used, these GaN crystals are heavy n-type, with the electron concentration of about $5 \times 10^{19} \text{ cm}^{-3}$ [5, 6]. Most likely, these electrons are related to substitutional oxygen in the N site of GaN lattice [7]. Therefore the problem of elucidation of the incorporation of oxygen in GaN crystals is interesting both from the point of view of fundamental research and of that of applications. The study of this process will be the main subject of this work.

Doping with group III metals during growth opens up the possibility of the compensation of these donors or even the crystallization of a p-type material. So far GaN crystals have been grown in the presence of Mg [8], Be [9], Ca [10], Zn [11] and Be together with Mg [12]. A variety of group II metal concentrations in liquid gallium have been used. As previously reported, Mg doping is the most efficient, allowing one to obtain semi-insulating or p-type crystals (after annealing). Be doping allows one to obtain highly resistive crystals. Doping with Zn and Ca allows one to reduce concentration of free electrons, but highly resistive or p-type crystals have not been obtained. Since these results been published in several papers [8–12], we present only a summary of recent results in this paper.

2. Cluster model of a liquid metal surface and the QM DFT calculation procedure

High-nitrogen-pressure solution growth (HNPSG) of GaN proceeds by dissolution of nitrogen in liquid Ga and diffusion to the cold end of the crucible where the growth from supersaturated solution takes place. The incorporation of oxygen requires, then, dissolution of oxygen in liquid Ga. A primary source of the oxygen is its trace concentration in the nitrogen gas used in the growth. Despite the fact that the concentration of oxygen is low, compression of the gas to 15 kbar increases its partial pressure. An even more important source of the oxygen contamination is related to that adsorbed on the surfaces of the growth apparatus. In the initial growth stage, annealing of the chamber takes place and the gas is pumped out to very low pressures. Some amount of oxygen and water remains adsorbed on surfaces, which cannot be heated to high temperatures. During heating to the growth temperature, these adsorbed quantities of oxygen and water can desorb and find their way to the Ga surface. Therefore, description of the oxygen dissolution in liquid gallium is very important for the high-pressure growth of GaN crystals.

The cohesion energy of a metal, originating from the attractive force between free electrons

and the positively charged atomic cores, can be relatively large, as shown by large heats of evaporation, for example 2.8 eV/atom for Ga [13]. The attraction is balanced by a screened electrostatic repulsion of the atomic cores [14]. In the case of simple metals, such as group III elements, the ion–ion interactions are pairwise and isotropic [14], therefore the group III metal crystals are soft and have relatively low melting temperatures (e.g. for Ga, $T_{Ga}^M = 302$ K). The electronic and optical properties of the liquid and solid phases are very similar, therefore processes entailing the creation of surface bonds and rearrangement of electronic charge distribution can have some degree of similarity.

For calculation of the dissolution energy barriers, the application of the adiabatic approximation is necessary. The validity of this approximation is especially crucial for surfaces of the liquids, where the thermal motion of atoms plays a very important role. The importance of the thermal motion of the liquid atoms depends on the ratio of the energy of bonding of adsorbed atoms to the surface and the average energy of the atomic motion. As was shown in [15], the adiabatic approximation can be used for nitrogen, where the energy barriers for N₂ dissociation are greater than 3 eV, far exceeding the average energy of thermal motion.

In contrast to the case of nitrogen, as will be shown below, due to much lower binding energy of oxygen molecule the dissociation of oxygen on a metal surface proceeds without an energy barrier. The binding energies of single O atoms to a metal surface are very high. In particular, for Al it is higher than 6 eV and for Ga it is higher than 3 eV. The energy of thermal motion can be neglected because it cannot contribute to the barrier height on the one hand and it cannot affect final adsorbed state of a single O atom on metal surface on the other.

In addition, thermal motion can cause creation of the instantaneous configuration of atoms of the metal, which is not beneficial for the dissociation of the oxygen molecule. The importance of such configurations depend on relative rate of change of the configuration and the duration of the collision process. For a low gas density, these rates are determined kinetically. For high pressures, however, the O₂ molecule is caught in a cage of neighbouring nitrogen molecules, which does not allow it to leave the surface too quickly. Therefore an O₂ molecule stays quite a long time at the metal surface. During this time, i.e. before the oxygen leaves the surface, the surface atoms have enough time to rearrange, so that the beneficial surface configuration can be attained. Therefore the existence of these adverse configurations can be neglected in analysis of high-pressure growth processes.

At present, the two approaches are used for the description of the adsorption processes: the first is the finite cluster model, which can include the embedding potential, and the second is supercell geometry [16]. According to a review [16], the relative merits of these approaches are still under investigation. In our calculation we follow the standard finite cluster approach [17]. This is the standard procedure used for calculation of chemisorption on solid surfaces [18]. The literature regarding the cluster approach to solid surfaces is very extensive and cannot be reviewed here (see, e.g., extensive literature review in [17]).

The isotropic metal–metal interaction leads to close packing of metal atoms in the configuration of minimal energy. Therefore in our cluster calculations, metal atoms (Al, Ga or In) are arranged in one or several layers of a hexagonal close packed lattice. The distances between the metal atoms in the cluster were obtained by minimization of the total energy. The obtained distances were 2.70 Å, 2.71 Å and 2.80 Å for Al–Al, Ga–Ga and In–In, respectively, which are in good agreement with the estimated metal–metal distances following from densities of liquid metals. The clusters consisting of single layer are labelled by a single number which is equal to the number of atoms in the cluster whereas the double layer clusters are labelled by the sum of two numbers, denoting the number of atoms in the first and second layer, respectively.

The potential energy barriers were calculated using the adiabatic approximation in which a single N atom, or O₂ molecule was shifted along the line perpendicular to the surface. The

metal atoms in the first layer of the cluster could relax their position in the surface plane, but the plane was kept flat, i.e. they could not leave the plane. The atoms in the second plane could relax their position with no constraints.

The quantum mechanical (QM) many-body Schrodinger equation was solved using a density functional theory (DFT) formalism, based on the Hohenberg–Kohn [19] and Kohn–Sham theorems [20]. The equations were solved using commercial DMol package [21] developed by MSI Inc. In the DFT approximation the multidimensional linear wavefunction equation is replaced by nonlinear equations for electron density. This transformation is exact to all terms except the exchange and correlation terms which cannot be expressed directly by the electron density. These terms were expressed using the Becke approximation for the exchange energy and Lee, Yang, Parr (LYP) approximation for correlation energy, respectively [22, 23].

The electronic wavefunction can be expressed in spherical coordinates (r, θ, ϕ) as a sum of products of radial function and spherical harmonics: $\Phi(r, \theta, \phi) = \sum_{l,m} R(r)Y_{lm}(\theta, \phi)$. In the DMol package the spherical harmonics $Y_{lm}(\theta, \phi)$ are calculated using an efficient numerical integration scheme based on a finite number of points, whereas the radial function $R(r)$ was calculated numerically as a spline function of the third-order on a grid in one-dimensional space [21].

The nonlinear matrix equations were solved using iterative procedure in a Newton–Raphson scheme. During iterations, the metal atom positions were relaxed to reach the minimum energy. The iteration/relaxation procedure was terminated after the two following conditions were fulfilled simultaneously: the electron density matrix norm change was smaller than 10^{-4} and the energy change was below 2×10^{-5} Ha. In most of the calculations, up to 12 iterations were needed to reach convergence. When the arrangement of the atoms was changed, for example during dissociation of the O₂ molecule, the number of required iterations was more than about 20.

3. Results of QM DFT calculations—dissolution of the oxygen in group III metals

3.1. Single O atom

As shown in [15], the asymptotic results describing the dissolution of nitrogen in liquid Al were obtained for clusters consisting of more than 27 Al atoms (see figure 1). Therefore adsorption and dissolution of single O atoms in liquid Al was analysed using relatively large clusters. The results obtained for a single O atom, presented in figure 2, are essentially similar to those obtained for nitrogen and Al. For O–Al(l) distances larger than 0.8 Å, the (27 + 18) Al atom cluster has sufficient size to represent the infinite liquid Al surface. However, calculation of the dissolution barrier requires the use of larger clusters—in fact for oxygen the asymptotic regime was not reached even for cluster consisting (48 + 36) Al atoms.

The results indicate that than oxygen atom is attracted very strongly by aluminium surface—the minimum of the excess energy is 6.2 eV. The dissolution barrier is very high, larger than 3.3 eV for the 48 + 36 Al cluster. This indicates that the dissolution of oxygen in liquid Al proceeds exclusively by a self-diffusion mode, i.e. by irregular slow wandering of the cluster consisting of the O atom and the surrounding metal atoms into the interior of the liquid metal. An alternative way of transition by a direct jump into the liquid can be neglected. The first dissolution can be realized only for surfaces of the liquids. For solids, only the second mode is possible. The results explain why a solid Al surface is passivated by an oxide layer whereas oxygen can be dissolved in liquid Al quite efficiently.

The results obtained for liquid aluminium, gallium and indium, presented in figure 3, indicate that both Ga and In surfaces also attract O atoms quite strongly (about 4.0 eV for

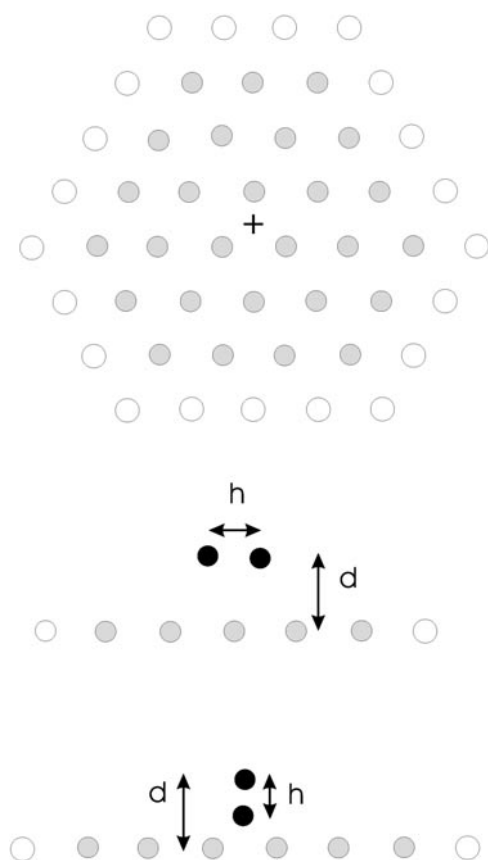


Figure 1. One-layer clusters used in the QM DFT calculations: upper part, top view; lower parts, side views with the O_2 molecule is oriented parallel and perpendicular to the surface. The grey circles denote 27 metal atoms, the white circles denote an additional 21 atoms, together giving 48 atoms; and the black circles denote O atoms. The cross denotes the location of the O_2 molecule.

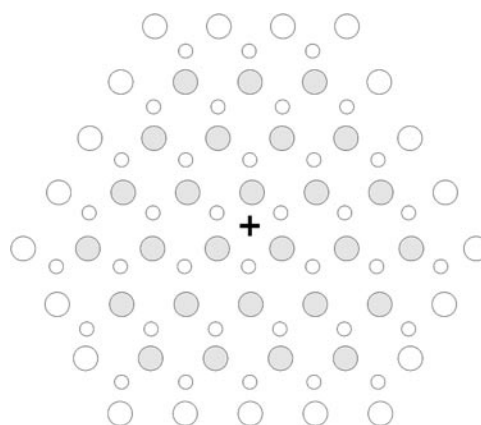


Figure 2. Two-layer cluster used in the QM DFT calculations: the larger circles denote the first layer and the smaller circles denote the second layer. The meaning of the shading and the cross are as in figure 1.

both Ga and In). The attractive energy is much lower than for Al (6.2 eV) showing that the adsorption of single oxygen atoms on Ga and In surfaces results in smaller energy gains.

3.2. O_2 molecule—parallel configuration

The calculation results obtained for an O_2 molecule oriented parallel to a liquid group III metal surface indicate that the O_2 molecule dissociates during the adsorption stage. The excess energies and O–O interatomic distance are presented in figures 4(a) and 4(b), respectively. A minimum of 0.2 eV of the excess energy of an O_2 molecule and Al surfaces is obtained for the distance $d = 2.0 \text{ \AA}$. This indicates the possibility of molecular adsorption of O_2 on an Al surface. The change of the excess energies for gallium and indium surfaces were smaller than the precision of the calculations.

The O–O interatomic distance increases moderately when the distance between the molecule and the surface is decreased to 1.8 \AA for Al and Ga and to 2.0 \AA for In. At the above

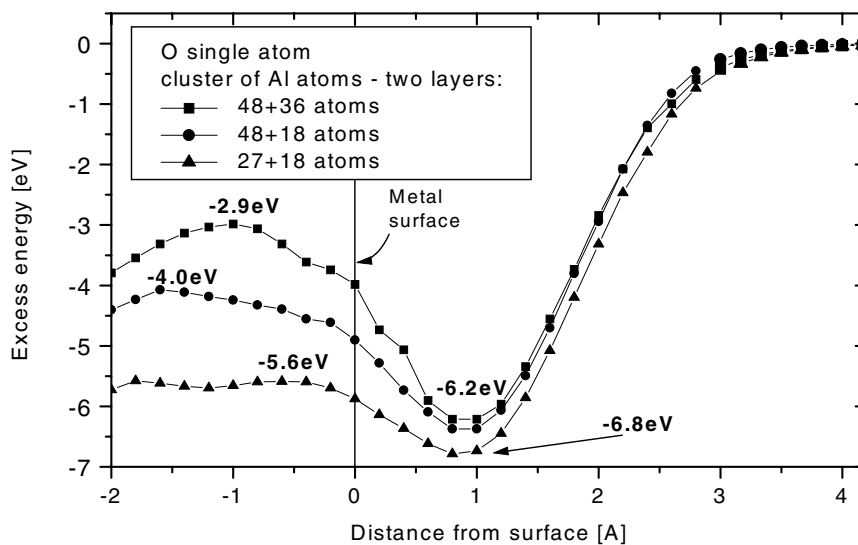


Figure 3. Excess energy of the system consisting of an O atom and an Al cluster as a function of the distance between the O atom and the Al surface and for various sizes of the system.

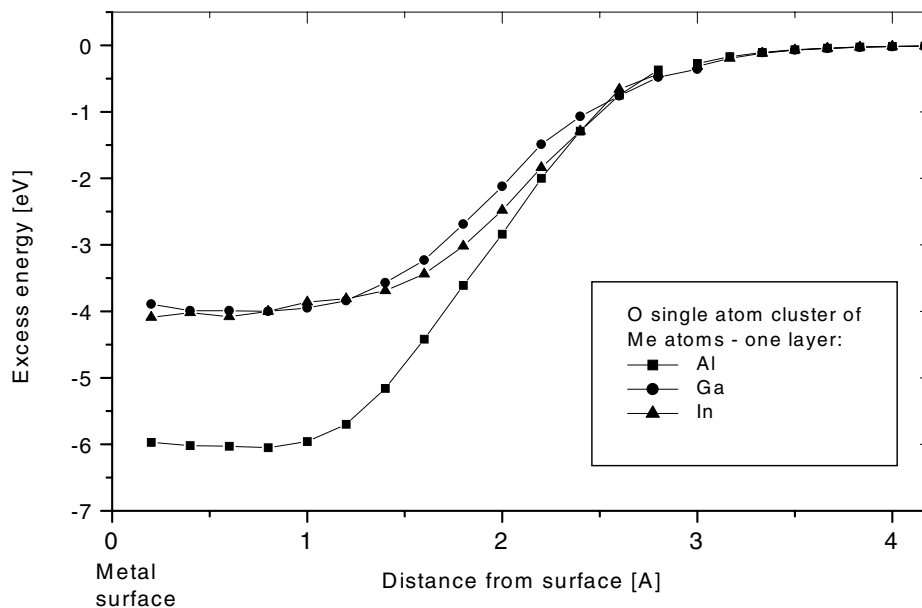


Figure 4. Excess energy of the system consisting of an O atom and single-layer metal (Al, Ga or In) cluster as a function of the distance between the O atom and the metal surface.

specified distance, a sudden increase of the O–O interatomic distance to about 3.5 Å is observed, which indicates on the dissociation of the oxygen molecule. This is confirmed by the shape of the excess energy curves, which closely resemble those obtained for single oxygen atoms for small distances. The energy minimum is equal to 7.5 eV. Adding 5.08 eV of the O₂ dissociation energy and dividing by two gives a 6.3 eV energy gain on the adsorption for a single O atom, which is in excellent agreement with the 6.2 eV obtained for a single O atom. We conclude that

the adsorption of molecular oxygen on liquid group III metal surfaces leads to the dissociation of the oxygen molecule. These oxygen atoms interact independently with Al surface.

In contrast to the N_2 molecule [15], the O_2 dissociation process is characterized by the absence of an energy barrier. The depth of the well corresponding to the oxygen atoms bound to the surface strongly depends on the metal involved: 1.8 eV for In, to 3.8 eV for Ga and 7.5 eV for Al. Also, the equilibrium distances differ: 0.4 Å for Al, 0.8 Å for Ga and 1.2 Å for indium.

Remarkably similar results were obtained by QM DFT calculation for the adsorption of oxygen on GaN surfaces [24, 25]. As shown before [26], both (0001) and (000 $\bar{1}$) GaN surfaces are gallium terminated and demonstrate metal-like properties. Therefore the electronic process have a high degree of similarity. The results of the calculation confirmed that: on both GaN faces O_2 adsorption leads to dissociation of molecules without an energy barrier [24, 25].

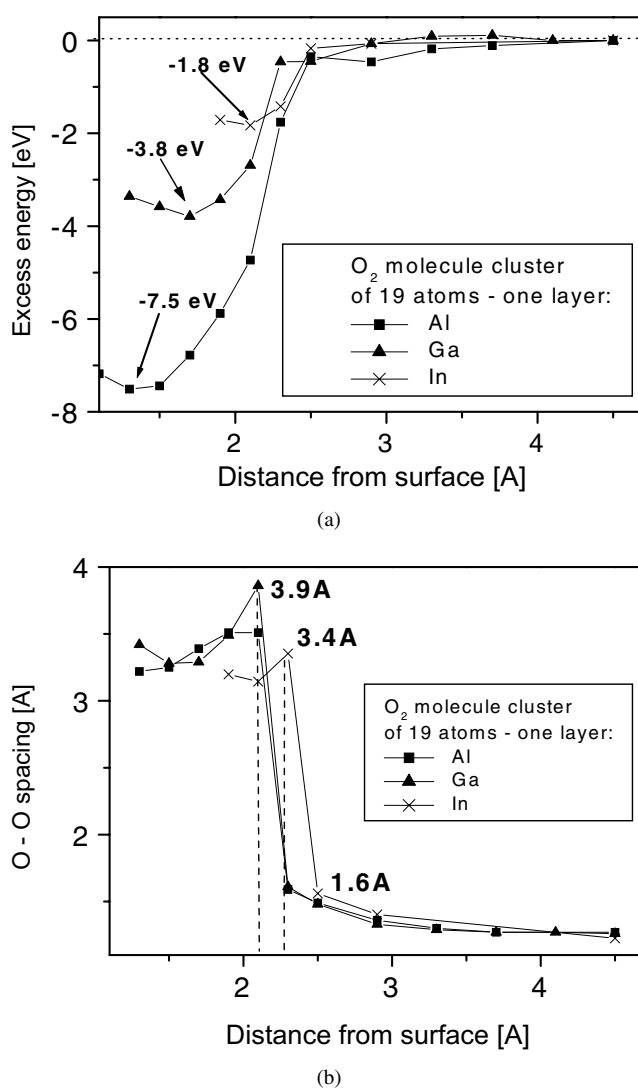


Figure 5. Results of the QM calculations for an O_2 molecule oriented parallel to the surface: (a) excess energy of the system, (b) distance between the O atoms as a function of the distance between the O_2 molecule and the metal surface.

3.3. O_2 molecule—perpendicular configuration

The calculations were also conducted for the adsorption of an O_2 molecule oriented perpendicularly to the liquid surfaces of Al, Ga and In. The results presented in figures 5(a) and 5(b), which include the excess energies and O–O spacing, show remarkable similarity to the parallel orientation. The adsorption process is dissociative with no energy barrier. Again the energy minimum corresponding to the molecular adsorption of O_2 on liquid Al was obtained. In contrast to earlier results, however, the same phenomenon is obtained for the adsorption of O_2 on liquid Ga and In surfaces. The difference obtained for Ga and In can be also caused by the fact that the energy of molecular adsorption states is much higher and easier to detect within the precision of the calculations. The minimum energy depends on the metal involved and is equal to 1.4 eV for Al, 1.0 eV for Ga and 0.6 eV for In. The barrier for the transition from a molecular O_2 surface state to the state of two single adsorbed oxygen atoms is very low: 0.2 eV for Al and Ga and 0.6 eV for In. Altogether the barrier energy level lies below the far distance value, which indicates that the existence of the molecular adsorption state influences the desorption process only. The energies of the adsorption states for close distances follow the curves obtained for a single O atom for all these surfaces: Al(l), Ga(l) and In(l).

4. Intentional doping by group II impurities

Doping by acceptor impurities has been conducted using Mg, Be, Ca and Zn [8–12]. The doping procedure depends on the dopant. The first stage requires dissolution of the dopant in liquid Ga. The dissolution of Mg in Ga requires annealing at a high temperature, where a nitrogen atmosphere can be used. For Be one has to use Ar because beryllium reacts with nitrogen, giving Be_3N_2 which is very stable and does not dissolve in liquid Ga. The dissolution procedure, similar to Be, was adopted for Ca. Zn can be added in a way similar to Mg.

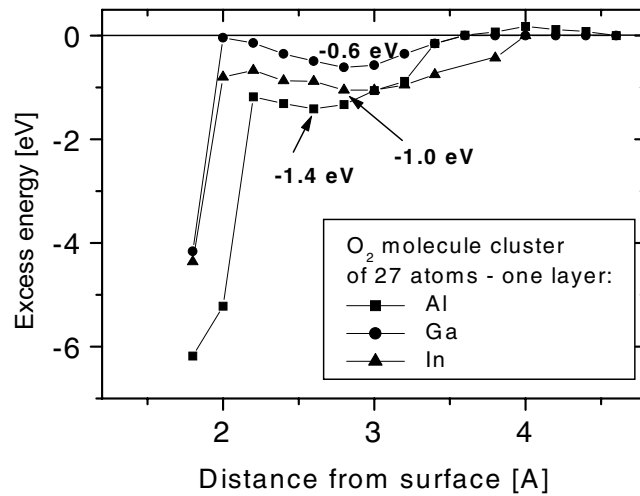
Results of the growth experiments depend on the concentration of the dopant in the liquid Ga. As a rule, for low concentrations, n-type GaN crystals are obtained. Adding more of the group II metal changes the electric properties. For Be and Mg, using concentrations higher than 0.5 at% leads to semi-insulating GaN crystals [8, 9]. For Ca and Zn, however, even use of relatively high concentration of the dopant, in excess of 5 at%, leads to a small decrease of the concentration of the electrons only [10, 11]. No p-type or semi-insulating GaN crystals were obtained.

The annealing procedure does not change the electric and optical properties of Zn-, Ca- and Be-doped GaN crystals [8]. In contrast, Mg-doped crystals change their properties. Two types of the behaviour of the semi-insulating crystals were observed: the first shows the dominance of the shallow and the presence of the deep levels and the second shows the dominance of the deep levels only. The shallow acceptor level has a hole activation energy close to 150 meV. The Mg acceptor shallow level can be activated by annealing in temperatures below 500 °C [12]. The other samples indicate the presence of the deep level of the activation energy, measured by the temperature change of the resistivity, of about 0.9 eV [12]. The deep level can be activated by annealing at a temperature above 650 °C. The nature of the level is still under investigation.

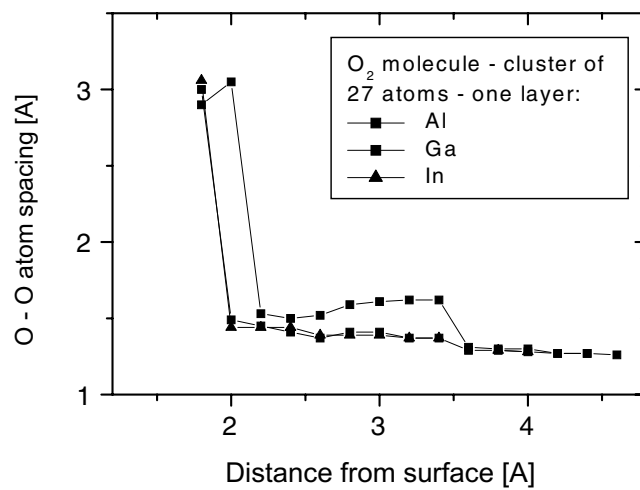
5. Summary

The results reported in this paper can be summarized as follows.

- (a) The adsorption of an oxygen molecule on a group III metal surface leads to dissociation of the oxygen molecule and creation of two independent O atoms attached to the metal surface.



(a)



(b)

Figure 6. Results of the QM calculations for an O_2 molecule oriented perpendicular to the surface: (a) excess energy of the system, (b) distance between the O atoms as a function of the distance between the O_2 molecule and the metal surface.

- (b) The dissociation of an oxygen molecule during adsorption is a barrierless process.
- (c) The energy barrier for a direct jump of an oxygen atom from the surface into the interior of a liquid group III metal is higher than 3 eV. Therefore the direct jump process is very slow at temperatures up to 2000 K.
- (d) The incorporation of oxygen into liquid group III metals proceeds by Brownian motion of clusters consisting of O atoms and surrounding metals atoms.
- (e) These results are consistent with the well known phenomenon of the rapid oxidation of a solid Al surface that then prevents further oxidation of the metal.
- (f) Mg doping during growth of GaN crystals by HNPG allows one to obtain:
 - semi-insulating and p-type GaN crystals;

- inversion of the growth morphology of GaN plate-like crystals;
 - properties of Mg-doped crystals which strongly depend on annealing.
- (g) Be doping during growth of GaN crystals by HNPG allows one to obtain:
- semi-insulating GaN crystals;
 - properties of semi-insulating GaN crystals do not depend on annealing.
- (h) Zn and Ca doping leads to a slight decrease of the concentration of free electrons in GaN crystals—no semi-insulating or p-type crystals have been obtained.

Acknowledgments

The research presented in this paper was supported by Poland's Committee for Scientific Research, grants 7 T08A 015 18 and 2 P03B 025 17.

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