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Nitrogen vacancy and oxygen impurity in AlN: spintronic quantum dots

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Point defects with non-zero spin are prototypical spintronic quantum dots. Here two anion-site defects in AlN are studied intensively in terms of their spin and related properties. The charged states of the nitrogen vacancy and substitutional oxygen impurity, in both ground and spin-flip states, are analyzed. The theoretical analysis includes optical absorption and emission, diffuse excited states, spin densities and local mode force constants. The relevance to spintronic quantum dots in semiconductors is discussed.

Keywords: point defects; aluminum nitride; spintronic systems; quantum dots

1. Introduction

The motivation for this work is well described in the announcement for a recent APS focus session on dopants and defects in semiconductors, namely, "The control of defects and impurities is the critical factor that enables a semiconductor to be used in electronic and optoelectronic devices. . . The fundamental understanding, characterization and control of defects are proving to be important for the development of novel wide band-gap semiconductors and future solid-state based spintronic devices" (*1*).

Aluminum nitride (AlN) is by now much studied as an optoelectronic material and as a high-temperature high-field semiconductor. Computational and theoretical analysis is also well advanced. In a recent paper, we presented the results of a computational study of charge states of the nitrogen vacancy v_N calculating its ground state configuration and optical excitations in the majority spin manifolds (*2*). In an important earlier work, Stampfl and Van de Walle (*3*) included some of the defect states using the periodic supercell approach in the framework of density functional theory. For some results on anion-site defects v_N and O_N in AlN, see (*4–8*), for example, reporting the atomic structure and formation energies.

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The present work carries out a much more comprehensive analysis applied not only to v_N but also to the oxygen substitutional impurity O_N. This is of practical importance in identifying defects, the properties of which show up in experimental studies because oxygen is ubiquitous. For both defects, the study is extended to charge state zero, which is likely to dominate or play a vital role in many thermally and chemically dependent properties. Similarly, the spin splitting of the optical transitions for a defect of a given charge and non-zero spin is expected to be observed. Furthermore, analysis of spin-flip states for a given defect becomes of interest as powerful optical and other techniques combine with the study of the magnetic, electrical and optoelectronic properties of wide band-gap semiconductors. We also present the results of a few calculations of optical emission energies and of a study to assess the diffuseness of excited electronic states in AlN. The calculations include in all cases the nearest-neighbor atomic displacements and spin densities, as well as effective breathing-mode force constants. In principle, one may expect the calculated results herein to help distinguish experimentally among different spin states, thereby contributing to defect characterization and to identifying processes of interest for technological development. We shall see that our results support this expectation in most cases. The current surge of interest in spin-dependent properties of defects and dopants in semiconductors brings new attention to all of the properties mentioned above.

In Section 2, we briefly describe our model and computational method. In Section 3, we give our results, with some discussion. In Section 4, we summarize the work in relation to the field of spintronic quantum dots.

2. Model and computational method

In (*2*), we have described and discussed in considerable detail the model and method used both as to generalities applicable to wide band-gap insulators and as to specifics of anion-site defects in AlN in the zincblende structure. We therefore give only a brief summary here. Our model of the defect crystal consists of a nearest-neighbor cluster of atoms centered on the defect site, embedded in a shell-model representation of an infinite crystal, The defect cluster is analysed in terms of bare nuclei and a set of electrons treated in self-consistent field unrestricted Hartree-Fock (UHF) approximation with second-order Rayleigh–Schrödinger many-body perturbation theory correlation correction. The Fock states are represented as LCAO-MOs. The partly covalent nature of AlN dictates that the shell-model ions of the embedding region be fractionally charged, ± 2.41 (units of proton charge $e > 0$). The polarization of the shell-model ions and of the crystal as a whole (for charged defects) is induced by point-charge simulators placed at atomic and defect sites within the cluster region to represent approximately the charge distribution of the quantum–mechanical solution. Specifically, a single point-charge simulator is determined for the defect site, while those at the nearest-neighbor Al sites maintain the correct defect charge value.

For ground and relaxed excited states (RESs), the total energy of the defect crystal is minimized self-consistently among the following elements: the UHF molecular cluster solution; the shell-model core and shell displacements due to the defect; part of the defect site basis set; nearest-neighbor displacements due to the defect. For unrelaxed states (excited states in optical excitation and ground states in optical emission), the UHF solution is obtained in the presence of atomic displacements and polarizations as determined in the appropriate stationary state.

3. Computed results

We now present computed results for the following defect properties: (1) the ground-state spin with spin stabilization energies; (2) the optical excitation energy ΔE and, for non-zero spin,

Table 1. Computed ground state spins S (units $\hbar$) and stabilization energies E_s (units eV) relative to lowest adjacent spins, for v_N and O_N in zincblende AlN, for defect charge states n (units $e > 0$), with correlation correction.

Nitrogen vacancy (v_N)			Oxygen dopant (O_N)		
n	S	E_s	n	S	E_s
0	3/2	1.40	0	1/2	2.00
1	1	1.00	1	0	3.67
2	1/2	2.44	2	1/2	13.72
3	0	4.14	3	0	11.94

the spin splitting; (3) the optical emission energy and Stokes shift ΔE_s; (4) nearest-neighbor displacements; (5) effective local breathing-mode force constants; (6) electron spin densities $\rho(\vec{r})$and Mulliken populations (MPs) at nearest-neighbor nuclear positions; (7) diffuseness of defect excited electronic states.

3.1. *The ground state spins and spin-state stabilization*

For each of the two defects v_N and O_N, we have examined the two lowest-spin states for each of the four charge states 0, 1, 2 and 3. For a given defect and a given charge, the spin eigenstate with lowest energy is the ground state. The difference between the ground state and the spin-flip excited state is the spin-state stabilization energy. These data are given in Table 1. For v_N, we find that the ground-state spin rises linearly as the charge decreases and the strength of the potential well for the vacancy-bound electrons diminishes. For O_N, the picture is quite different, with the lowest spin (maximum pairing) prevailing at all charge values studied, and large (> 10 eV) stabilization energies for charges 2 and 3. Overall, the stabilization energies are at least 1 eV. The totality of these results indicates that there are rich opportunities for experimental identification and manipulation of spins in these defects. The energies used here, and for all optical quantities below, are for pure-spin states and include second-order many-body perturbation theory correlation corrections to self-consistent field UHF approximations.

3.2. *Optical excitation with spin splitting*

Optical excitation (absorption) energies ΔE for all charge and spin states studied are given in Table 2. For non-zero spin states, the occupancies of the two spin manifolds spin "up" and spin "down" are different, and therefore the energies for excitations taking place in the two manifolds are unequal, resulting in a splitting of the absorption line. Not all conceivable data were obtained in Table 2: for O_N, positions occupied by a dash indicate that the necessary excited state calculation could not be made to converge; for v_N, positions occupied by a star indicate calculations that converged to unphysical solutions.

The band gap in AlN is about 6 eV. For v_N, most of the calculated absorption energies are less than or close to this, suggesting a true defect process. For two or three, particularly $n = 3$, $S = 0$, the result suggests a transition largely to the conduction band. For O_N, because of convergence difficulties, the overall picture is not well-defined, but a great number of computed transition energies are well above 6 eV. The question of highly diffuse excited states is addressed in Section 3.7.

3.3. *Optical emission and Stokes shift*

Following absorption in the ground-state configuration of the crystal, the excited state and the crystal come to equilibrium in the RES. This process is followed by emission, taking the system

Table 2. Computed optical excitation energies ΔE (units eV) in majority and minority spin manifolds and spin splittings (eV) of the absorption lines for defects v_N and O_N in zincblende AlN, for defect charge states n (units $e > 0$) and spins S (units $\hbar$), with correlation corrections.

Nitrogen vacancy (v_N)					Oxygen dopant (O_N)				
N	S		ΔE	Split	n	S		ΔE	Split
0	3/2	Maj	7.43		0	1/2	Maj	–	–
		Min	5.52	1.91			Min	5.00	–
	1/2	Maj	2.51			3/2	Maj	–	
		Min	2.28	0.23			Min	9.80	–
1	1	Maj	2.15		1	0		6.18	0
		Min	4.59	2.44		1	Maj	2.73	
	0		1.48	0			Min	10.87	8.14
2	1/2	Maj	3.04		2	1/2	Maj	7.90	
		Min	6.75	3.72			Min	12.29	4.39
	3/2	Maj	2.22			3/2	Maj	–	
		Min	*	*			Min	–	–
3	0		13.62	0	3	0		14.02	0
	1	Maj	3.29			1	Maj	–	
		Min	*	*			Min	6.97	–

Table 3. Emission energies $\Delta E'$ (units eV) and Stokes shifts (eV) for selected v_N and O_N defects in zincblende AlN, in charge states n (units $e > 0$) with spins S (units $\hbar$), excited in majority or minority spin manifolds, with correlation correction.

Nitrogen vacancy (v_N)					Oxygen dopant (O_N)				
n	S		$\Delta E'$	Stokes	n	S		$\Delta E'$	Stokes
0	3/2	Maj	6.66	0.77	1	1	Maj	2.56	0.17
		Min	4.85	0.70	2	1/2	Min	6.22	1.68

to the unrelaxed ground (UNRG) state, which subsequently relaxes to the relaxed ground (G) state. (The final state of absorption is called the unrelaxed excited state, UNRES.) The difference between excitation and emission frequencies is called the Stokes shift. In Table 3, we give the emission energy and Stokes shift for a few selected cases from Table 2.

The ground-state relaxation will be discussed in Section 3.4. It is found that the RES electronic configuration is unsymmetrical, and therefore the nearest-neighbor atomic displacements will be also. We did not undertake to determine this asymmetry, but limited the relaxation to displacements that are equal for all four nearest-neighbor Al ions. We see that even with symmetrical relaxation, some substantial Stokes shifts are obtained. Note that the Stokes shift is perceptibly differentiated even between excitations in the majority and minority spin manifolds for v_N^0, $S = 3/2$. These are the first computational modeling estimates at the embedded molecular cluster level that we are aware of for Stokes shifts.

3.4. ***Nearest-neighbor displacements***

Fractional nearest-neighbor displacements in relaxed ground and excited states are given in Table 4. We see that for vacancy states the displacements are in the range 10–20% outward,

Table 4. Fractional equilibrium displacements δ and δ' for ground and RESs respectively of nearest-neighbor Al ions of v_N and O_N in zincblende AlN, for charge states n (units $e > 0$) and spins S (units $\hbar$), and ground-state effective local breathing-mode force constants K (units eV $\cdot a_0^{-2}$).

Nitrogen vacancy (v_N)						Oxygen dopant (O_N)					
n	S	δ	K	δ'		n	S	δ	K	δ'	
0	3/2	0.140	59	0.100	Maj	0	1/2	−0.020	83		
				0.190	Min		3/2	0.014	65		
	1/2	0.138	55								
1	1	0.126	47			1	0	−0.022	91		
	0	0.126	48				1	−0.006	86	0.008	Maj
2	1/2	0.030	66			2	1/2	−0.006	108	0.034	Maj
	3/2	0.176	47				3/2	0.080	73		
3	0	0.040	58			3	0	0.008	93		
	1	0.090	58				1	0.074	76		

while for oxygen they are generally much smaller, $\leq 2\%$, two exceptions being spin-flip excited states.

3.5. *Effective local breathing-mode force constants*

The effective force constants K for n.n. displacements in equilibrium with the rest of the crystal are also given in Table 4. The results are with symmetrical displacement (whence "breathing-mode") at the UHF level. They are evaluated using a parabolic fit to the curves of total energy vs. n.n. displacement, with excursions limited to a few percent. We see that the values of K for O_N are on average about 65% higher than those for the vacancy defect, with easily perceptible differences between different states and between different spins for a given defect charge.

3.6. *Electron spin densities and MPs*

Electron spin densities $\rho(\vec{r})$, evaluated at nuclear positions, relate directly to isotropic hyperfine constants. Qualitatively, for v_N, the calculated values at n.n. Al nuclei are in the range 0.006–0.3 ($\hbar a_0^{-3}$). For O_N in charge states 0 and 2 with spin 1/2, the values are 0.04 and 1.5, respectively, with values in the 1.1–1.5 range for the spin-flip excited states. The corresponding values at the n.n. Al nuclei are 125 and 1.7, respectively, with values around 120 for the spin-flip states with one exception. Full details in tabular form are available from the authors. Such details are of interest for spintronic applications to quantum computing, where hyperfine coupling contributes to spin relaxation and decoherence (*9*).

MPs are a measure of the total number of electrons associated with a given nuclear or defect site. In covalent materials, this measure is of particularly limited value. The following comments are subject to this limitation. For v_N, we find the ground state values of the n.n. Al ions ranging from 10.0 down to 9.7 as electrons are added to go from charge states 3 to 0: that is, the ionic charge has the filled-shell value of +3. In the vacancy site, the added electrons align successively to give spins 1/2, 1 and 3/2 for $n = 2$, 1 and 0, upon a spin-paired couple of electrons at $n = 3$. For O_N, the ground state MPs for the nearest Al ions range from 10.1 up to 11.0 as n goes from 3 down to 0. For the oxygen ion, the corresponding values are 9.5, 9.3, 9.2 and 9.2, all closer to ionic charge −1 than to the filled-shell value of −2. At each value of n, spin pairing is maximal (Table 1). The successive spin alignments of v_N in the vacancy, maintaining ionic charge +3 for n.n. Al ions, and the persistent oxygen charge −1 with maximum pairing for O_N, are principal features of this defect system. Again, full details in tabular form are available.

3.7. *Diffuse excited electronic states*

It can happen that the electronic structure of a point defect overlaps a large number of atoms in the crystal but is still localized. The method used here is not capable of modeling such a situation because ions beyond nearest neighbors are represented by point charges in the shell model. In an earlier publication (*10*), we showed how to correct calculations of the sort done here for the case of diffuse states. The first step in that procedure is to see whether the electrons at the top of the valence band (occupied manifold) reduce the total energy of the defect crystal, relative to that of the angstrom-scale localization determined here, when they are allowed to spread out into the surrounding crystal. That is, we check to see if the total energy has a lower minimum with a diffuse excited-state electron. If it does, several corrections (*10*) are required for the model before a definitive comparison can be made between diffuse and atomic-scale cases of localization. We have applied the initial test to all UNRESs in Table 2 and to the RESs in Table 3. Among the four RESs considered, only O_N^{2+} with $S = 1/2$ and majority spin excitation is promising. Three other defects are also considered to be promising from UNRES results. They are O_N^{3+} with $S = 0$, v_N^0 with $S = 1/2$ and minority spin excitation, and v_N^{3+} with $S = 0$. Further analysis along the lines of (*10*) is justified for these four cases. Diffuseness is important because it affects all defect processes, some radically, as well as the defect–defect interaction. In particular, overlap between well separated defects may be important for some kinds of spintronic applications.

4. Spintronic quantum dots

Finally, some comments on the relevance of this work to spintronic quantum dots. All the properties computed in this work, except MPs, can in principle and frequently in practice be measured experimentally. They can be used to identify the defect charge and spin states since, in most cases (see the tables), different states are resolved by amounts well beyond normal experimental tolerances. Alternatively, if a particular defect states is found from the calculations to have a particularly desirable property from the viewpoint of technical application, then it may be possible to create it with dominant concentration in a material sample. In real materials, defects with non-zero charges are associated with other defects having equal and opposite charges. The present results apply only to cases where the defect and its charge-compensating defect are well dissociated. This will usually require special materials preparation.

In earlier work on point defects, spin-dependent properties have not been emphasized because until recently the value of basing devices on electron spin dynamics rather than charge dynamics has not been taken so seriously. More recently, the study of spin-based electronic processes, namely spintronics, has resulted in a wide range of new ideas, both fundamental and technological. Many of these ideas seek to exploit the spin of electrons in quantum dots; that is, electrons localized within nanometer dimensions. In a sense, the ultimate quantum dot is subnanoscale, namely angstrom scale, where localization is based on the atomic structure of the material – precisely the case for the defects studied in this work.

In one area at least, study of quantum dots for quantum computing (q-bits) has become a thriving research topic. That area is point defects in diamond, specifically the so-called Nv-N system (*11, 12*). This system consists of near-neighbor vacancy and substitutional N, with another free-standing N ion nearby. Among studies of defects in diamond, spin-flip and optical transitions figure strongly as processes that are involved in q-bit operation. The quantitative estimate for these processes has been emphasized in the present work.

Limitations in our model and computational method will need to be overcome for better quantitative results. This could be accomplished with more powerful Hartree–Fock software. Particularly, in the context of spintronic quantum dots, spin-orbit coupling analysis is desirable.

Nonetheless, we trust that the work serves to illustrate how useful this approach can be in the study of point defects in wide band-gap insulators, and that it serves as a baseline for expansion of the field.

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