

Doping-induced modulation of electrical and optical properties of silicon nitride

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Abstract

This work presents first-principles calculations of electronic structure and optical properties of doped α -Si₃N₄. It is found that B and P impurities form shallow acceptor and deep donor bands, respectively, in the band gap of α -Si₃N₄. Analysis of the charge neutrality level indicates that bipolar doping of α -SiN_x is possible and that both *n*- and *p*-type electrical conductivity can be expected. This result can be helpful to extend the list of device applications of SiN_x. Furthermore, it is shown that upon heavy doping with these impurities, the optical properties of the material are modified by doping. Both the refractive index and extinction coefficients are increased over the photon energy range 0-4 eV as a result of the doping.

Keywords: Silicon nitride doped by B and P, electrical and optical properties, band offset, charge neutrality level.

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1. Introduction

SiN_x has found extensive applications as an antireflection coating for modern Si solar cells [1-3]. This is a result of several advantageous properties of SiN_x, including a large fundamental band gap ($E_g > 3.5$ eV), a suitable refractive index of ~ 2.0 , a capability to supply a large amount of H for passivation of bulk and interface defects in the silicon solar cell, as well as its ability to form an excellent barrier against moisture and mobile ions. Many features of crystalline (*cr*) SiN_x, amorphous (*am*) SiN_x, and *am*-SiN_x:H are already well known. The band gap for α - and β -Si₃N₄ has been experimentally determined [4] from analysis of the soft x-ray emission spectra and is in the range 4.7-4.9 eV. The value of E_g for *am*-Si₃N₄ has been determined [5] from the energy loss spectra of N 1s photoelectrons and is ~ 5.4 eV. In the case of hydrogenated SiN_x, the experimental band gap for *am*-SiN_x:H is in the range 4.5-5.0 eV [6] for $x \approx 1.3$. Because of the large fundamental band gap, poor electrical conductivity and dopability by shallow level impurities, *am*-SiN_x can not be considered as semiconductor, it is rather a wide band gap insulator. The conduction band (CB) and valence band (VB) of *am*-SiN_x:H form large offsets with those of Si [7]. According to XPS studies [5], the offset between CB and VB of *am*-SiN_x and *p*-Si is ~ 2.38 eV and ~ 1.90 eV (Fig. 1 (a)), respectively. The offsets can be modulated by structural point defects. Despite the large band offsets with Si, *am*-SiN_x:H is widely used in Si based solar cells as antireflection coating, emitter passivation, diffusion barrier, etc [1-2, 8].

The influence of N deficiency on the electronic structure of SiN_x has been studied experimentally. From the core-level and VB photoemission studies it is found that upon increasing the parameter x in SiN_x in the range 1.00-1.33, the top of the VB of hydrogenated and non-hydrogenated SiN_x remains unchanged, whereas the bottommost

CB is increased (Fig. 1 (b)). However, the Fermi level (E_F) is found to be near the mid-gap [9]. These results indicate that the offset between CB and VB of *am*-SiN_x and Si increases with increasing the N content characterized by the parameter x up to $x \approx 1.33$. Since the thickness of the SiN_x layer used in conventional Si-based solar cells is ~ 20 nm [10], the large band offsets are not expected to be the main obstacle for current transport through the interface.

Doping of SiN_x and getting *n*- and/or *p*-type *am*-SiN_x or *am*-SiN_x based p-n junction would present interest because it would extend the list of applications of the material. One of the widely used impurities in SiN_x is H. However, H contributes to electrical conductivity through enhancing the passivation of bulk and surface defects. Its influence on electronic structure of SiN_x has been the subject of extensive experimental studies [11]. Although H is found to increase the band gap of Si rich SiN_x ($[N]/[Si] < 1$), its effect on E_g is negligible in N rich SiN_x ($[N]/[Si] > 1$), because both the bottommost CB and topmost VB are determined by N. Doping with B and P (Refs. [12-13]) as well as F have also been studied experimentally. However, these studies have been devoted to Si rich SiN_x with $x < 0.8$. There are no theoretical or experimental studies of influence of these impurities on electronic structure and optical properties of SiN_x with an N content in close vicinity of $x \approx 1.33$, which presents interest for solar cell applications of SiN_x. Furthermore, there is no discussion regarding dopability of *cr*- and *am*-SiN_x. The aim of the paper is to study doping-induced modulation of electrical and optical properties of hydrogenated and non-hydrogenated *cr*- and *am*-SiN_x.

2. Theory

We have considered the *cr*- and *am*- modifications of Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$. Structural information for *cr*- and *am*- Si_3N_4 as well as *cr*- and *am*- $\text{Si}_2\text{N}_3\text{H}$ used in the present work is reported in our earlier work (Ref. [14]). The amorphous lattices for hydrogenated and non-hydrogenated *am*- Si_3N_4 have been generated by two methods, namely *ab initio* molecular dynamics and CRAN [15-17]. The supercells for *am*- Si_3N_4 and *am*- $\text{Si}_2\text{N}_3\text{H}$ consist of 112 and 144 atoms, respectively. We considered two different phases of *cr*- Si_3N_4 . One is the β -phase with hexagonal structure, known as space group (SG) 176. The other is the α -phase with trigonal structure (SG 159). The orthorhombic phase of *cr*- $\text{Si}_2\text{N}_3\text{H}$ (SG 36) has also been considered. The materials *am*- Si_3N_4 and *am*- $\text{Si}_2\text{N}_3\text{H}$ possess P_1 symmetry.

The band structure calculations have been performed using the VASP-PAW package [18-19], which calculates the Kohn—Sham eigenvalues in the framework of the density functional theory (DFT) within the local density approximation (LDA). The exchange and correlation energy per electron were described by the Perdew-Zunger parametrization [20] of the quantum Monte Carlo results of Ceperley-Alder [21]. The interaction between electrons and atomic cores was described by means of non-norm-conserving pseudopotentials implemented in the VASP package. The pseudopotentials are generated in accordance with the projector-augmented wave (PAW) method [22-23]. The application of the pseudopotentials allows us to construct orthonormalized all-electron-like wave functions for the Si- and P- $3s$ and $-3p$, B- and N- $2s$ and $-2p$, as well as H- $1s$ valence electrons. A plane wave cut-off of 500 eV is employed to ensure sufficient convergence for reproducing ground state properties. The convergence was assumed achieved when the forces acting on the atoms were smaller than $10 \text{ meV } \text{\AA}^{-1}$.

and the total energy difference between two consecutive iterations were $<10^{-6}$ eV. Spin-orbit coupling was not included in the present calculations.

Following Ref. [24], the charge neutrality level (CNL) has been used to characterize the doping of SiN_x phases. The CNL is identified as the stabilized Fermi energy E which has been calculated from the equality to zero of the real-space Green function G

$$G(E) = \int \int_{\text{BZ}-\infty}^{\infty} \frac{N(E')dE'}{E - E'} = 0, \quad (1)$$

where E' represent the eigenvalue and $N(E)$ is the density of states (DOS) obtained from the band structure calculations. The integration in Eq. (1) has been performed over the Brillouin zone (BZ) without correcting the band gap. In the examples of SnO_2 , CuAlO_2 , and CuInO_2 , it is shown [24] that the CNL value with respect to the CB and VB edges can be used as the measure of favourability of a solid for n -type, p -type or bipolar doping.

The imaginary part of the dielectric function $\varepsilon_2(\omega)$ was calculated by the DFT within the LDA and used to estimate optical properties, such as the absorption coefficient $\alpha(\omega)$, the reflectivity $R(\omega)$, as well as the refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ by the Kramers-Kronig transformation. More details of the computations of optical properties can be found in Ref. [14]. For all the structural modifications of hydrogenated and non-hydrogenated Si_3N_4 we have presented the results for the crystallographic direction perpendicular to the axis c .

As noted in our earlier study [14], the optical properties of the amorphous and crystalline phases of SiN_x are quite similar. Based on this finding, the studies of impurities have been performed for α - Si_3N_4 , but can be extrapolated for other structural

modifications of SiN_x as well. P and B impurities substituting Si have been considered in $2 \times 1 \times 2$ supercells of $\alpha\text{-Si}_3\text{N}_4$, which correspond to an impurity concentration of $8.4 \times 10^{20} \text{ cm}^{-3}$. The reason for the choice of B and P is that the background information about doping of Si rich SiN_x with these impurities is already available. Furthermore, SiN_x has been used in contact with n^+ and $p\text{-Si}$.

3. Results and discussion

In the analysis of dopability of the hydrogenated and non-hydrogenated SiN_x , knowledge of the CNL value can be useful, which can be calculated from electronic structure. Below we shall perform such analysis. Figure 2 demonstrates the total DOS for $\alpha\text{-}$ and $\beta\text{-Si}_3\text{N}_4$, $am\text{-Si}_3\text{N}_4$, $cr\text{-Si}_2\text{N}_3\text{H}$, and $am\text{-Si}_2\text{N}_3\text{H}$. General trends of the DOS agree well with the available theoretical results (see, e.g., Ref. [14]). The fundamental band gaps and CNL have been determined from the total DOS (Table 1). As expected, the calculated band gaps are underestimated compared with experimentally measured ones, due to well known deficiencies of DFT. The calculated band gaps of 4.6 eV for $\alpha\text{-Si}_3\text{N}_4$ and 4.2 eV for $\beta\text{-Si}_3\text{N}_4$ are smaller than the values of 4.7-4.9 eV, which have been determined [4] experimentally. The experimentally determined fundamental band gap of 5.4 eV of $am\text{-Si}_3\text{N}_4$ is larger than the calculated 4.3 eV. There are no experimental results for neither $cr\text{-}$ nor $am\text{-Si}_2\text{N}_3\text{H}$. The experimental band gap of $\text{SiN}_x\text{:H}$ is in the range 4.5-5.0 eV [25] for $x \approx 1.3$. Since Si, N, and H do not contain d electrons, band gap underestimations for all the SiN_x phases are not as severe as in transition metal compounds [26].

Below we shall study electronic structure of $\alpha\text{-Si}_3\text{N}_4$ with these impurities. Since, as noted in our earlier study [14], the optical properties of $am\text{-}$ and $cr\text{-SiN}_x$ are

similar to each other, the results of the present paper can be extrapolated to other structural modifications of SiN_x . Figure 3 presents the total DOS for B and P doped $\alpha\text{-Si}_3\text{N}_4$. Analysis shows that B forms a shallow acceptor level. Hence, it can enhance p -type electrical conductivity of SiN_x . However, P impurities form a deep donor band, which can enhance carrier recombination. As a result of the doping, the band offset between the B doped SiN_x and $p\text{-Si}$ would be reduced from 1.9 eV (Fig. 1) to 0.9 eV whereas the one between $n\text{-Si}$ and P doped SiN_x is expected to be reduced from 2.4 eV (Fig. 1) to 1.0 eV.

The impurities can modulate not only the electronic structure, but also optical properties of solids. Below, the optical properties of B and P doped $\alpha\text{-Si}_3\text{N}_4$ (Fig. 4) have been studied. It is found that the absorption coefficient and reflectivity are increased in the photon energy ranges 0.0-7.5 and 0.0-5.0 eV, respectively. However, at larger photon energies, both $\alpha(\omega)$ and $R(\omega)$ of the P and B doped $\alpha\text{-Si}_3\text{N}_4$ are smaller than those of undoped $\alpha\text{-Si}_3\text{N}_4$.

One of the most important optical parameters is the refractive index $n(\omega)$. The calculations performed in this work show that B doping only slightly increased $n(\omega)$ in the energy range 0.0-3.5 eV. However, it is drastically reduced for 4.0-12.0 eV, to only ~36% of the value of $n(\omega)$ for undoped $\alpha\text{-Si}_3\text{N}_4$. Upon doping by P, $n(\omega)$ increases. The largest increase corresponds to a value 33% higher than that of undoped $\alpha\text{-Si}_3\text{N}_4$. At energies >4.0 eV, the difference between $n(\omega)$ corresponding to B and P doped $\alpha\text{-Si}_3\text{N}_4$ is negligible. It should be noted that P and B doping of $\alpha\text{-Si}_3\text{N}_4$ also leads to a drastic increase of the extinction coefficient $k(\omega)$ in the photon energy range 0.0-7.0

eV. This will enhance the absorption of those photons in the α -Si₃N₄ layer, which is unwanted in conventional solar cell structures.

One of the important problems is related to dopability with impurities providing *n*- and/or *p*-type electrical conductivities. From DFT studies of electronic structure of solids, a qualitative solution of the problem can be obtained by analysis of the CNL (Table I). According to definition, if the CNL value is close to CB(VB) it might indicate dopability of a solid by the impurities providing both *n*- and *p*-type electrical conductivities. Here, this approach has been used for different structural modifications of SiN_x. For simplicity we have presented the relation of the CNL to the fundamental band gap in Fig. 5. The analysis of Fig. 5 shows that the value of CNL/ E_g is in close vicinity of 0.5. Consequently, SiN_x might be capable for bipolar doping, and both *n*- and *p*-type of electrical conductivity is expected in SiN_x. This result has technologically important implications. It shows that it should be possible to designing a fully SiN_x-based *p-n* homojunction. This question has not previously been discussed in the scientific literature, and should present interest for the semiconductor device industry. Devices based on SiN_x are expected to be mechanically strong, possess good dielectric properties, be stable to moisture, corrosion, mobile ions coming from the environment, etc.

Analysis of the above results indicates that the CB and VB offsets between Si and α -Si₃N₄ can also be modulated by B and P doping. However, heavy doping with concentrations of $\sim 10^{21}$ cm⁻³ severely modulate optical properties of the α -Si₃N₄ and it might become not attractive for applications as antireflection coatings. Smaller concentrations of B or P ($\sim 10^{15}$ cm⁻³) would not change the optical absorption and refractive index as much as they are in Fig. 4.

One interesting question to discuss is whether the SiN_x phases are capable of conducting electrical current. Preliminary theoretical studies of the band parameters, which are important to characterize electrical properties of SiN_x , are available. The effective masses of electrons and holes calculated [27] for α - and β - Si_3N_4 are of the same order as those for commonly used semiconductors. However, they are strongly anisotropic. Systematic theoretical and experimental studies of this issue are still needed.

Conclusion

From the study of the electronic structure and optical properties of *am*- and *cr*- Si_3N_4 , it is found that B and P form shallow acceptor and deep donor bands in the band gap of SiN_x . It is shown that upon heavy doping with these impurities, the absorption coefficient, reflectivity, refractive index, and extinction coefficient can be increased. At smaller concentrations of these impurities, the optical properties of SiN_x should be similar to those of undoped SiN_x . From the study of the charge neutrality level it is found that bipolar doping of SiN_x can be possible, i.e., both *n*- and *p*-type electrical conductivity is expected. If confirmed experimentally, this result can cause important device applications of SiN_x .

Acknowledgments

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Table 1. Fundamental band gap E_g and CNL calculated in the present paper along with those measured experimentally for crystalline and amorphous phases of Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$.

Compound	E_g (eV)		CNL (eV)
	Theory	Expt.	
$\alpha\text{-Si}_3\text{N}_4$	4.6	4.7-4.9 ^a	2.30
$\beta\text{-Si}_3\text{N}_4$	4.2		2.05
<i>am</i> - Si_3N_4	4.3	5.4 ^b	1.54
<i>cr</i> - $\text{Si}_2\text{N}_3\text{H}$	5.0		2.71
<i>am</i> - $\text{Si}_2\text{N}_3\text{H}$	4.8	4.5-5.0 ^c	1.76

^{a)} Soft X-ray emission spectra.[4]

^{b)} Energy loss spectra accounted from N 1s electrons.[5]

^{c)} Optical gaps determined[6] for $\text{SiN}_x\text{:H}$ from the transmission in the absorption edge and nearby regions using a DMR-21 Zeiss spectrometer.

Figure captions

Fig. 1. Schematic presentation of energy band diagram for the (a) heterostructure Si_3N_4 - $\text{Si}(100)$ (Ref. [5]) as well as (b) for VB and CB energies of SiN_x for $x=0, \dots, 1.33$ accounted from N 1s core level (Ref. [9]) determined from XPS studies.

Fig. 2. Total DOS for α - Si_3N_4 , β - Si_3N_4 , *am*- Si_3N_4 , *cr*- $\text{Si}_2\text{N}_3\text{H}$, and *am*- $\text{Si}_2\text{N}_3\text{H}$. The Fermi level is set to zero.

Fig. 3. Total DOS for B and P doped α - Si_3N_4 . The Fermi level is set to zero.

Fig. 4. Calculated absorption coefficient and reflectivity for undoped as well as for B and P doped α - Si_3N_4 . The absorption coefficients are given in $[\text{cm}^{-1}]$ divided by 10^5 .

Fig. 5. CNL over fundamental band gap ratio for α - and β - Si_3N_4 , *am*- Si_3N_4 , *cr*- $\text{Si}_2\text{N}_3\text{H}$ and *am*- $\text{Si}_2\text{N}_3\text{H}$.