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Comparative analysis of electronic structure and optical properties of crystalline and amorphous silicon nitrides

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We present a study of the electronic structure and optical properties of Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$ in crystalline and amorphous phases by first-principles calculations. We find that besides structural disorder those matrix atoms with dangling and floating bonds contribute to energy levels close to the Fermi level. From a comparative analysis of calculated optical spectra we conclude that the difference in optical properties between crystalline and amorphous silicon nitrides—either hydrogenated or unhydrogenated—is only small. It is present mainly in the energy range close to the fundamental band gap. At larger energies the difference is negligible. It is found that the structural disorder in silicon nitrides investigated does not affect essentially the electronic structure and optical properties of these materials. It is concluded that such amorphous silicon nitrides can be used instead of their crystalline counterparts for various applications in which optical properties of such materials are important. © 2009 American Institute of Physics. [doi:10.1063/1.3213359]

I. INTRODUCTION

Silicon nitride has found a wide range of applications in different fields as structural (automobile engines parts, cutting tools, and nuclear reactors) and electronic material (dielectric, Si based integrated circuits, and optoelectronics).¹ In semiconductor electronics $\text{SiN}_x\text{:H}$ prepared by plasma-enhanced chemical vapor deposition is widely used. Interest to $\text{SiN}_x\text{:H}$ is because it is mechanically strong, provides excellent barrier against mobile ions and corrosion, and can contain a large amount of H atoms, needed for passivation of bulk and surface defects, a large fundamental band gap (>3 eV), and low extinction coefficient.^{2,3} To improve the applicability of am- $\text{SiN}_x\text{:H}$ in electronics, however, a deeper understanding of its electronic structure and optical properties is needed both theoretically and experimentally. The scientific literature presents several theoretical and experimental studies of properties of crystalline (cr) and amorphous (am) phases of pure and defective, hydrogenated and nonhydrogenated silicon nitride materials (see Refs. 1 and 4–10). Core-level and valence band (VB) photoemission studies addressed the origin of the conduction band (CB) minimum and VB maximum as well as the influence of H on these parts of the electronic structure.⁴ Accordingly, N $2p$ states contribute most to the VB maximum of SiN_x for $x > 1.1$. However, if $x < 1.1$, then the VB maximum is dominated by Si $3p$ electrons. Similarly, the CB minimum is determined by Si $3s$ electrons for $x < 1.25$, while hybridized Si $3s$, $3p$, and N $2p$ states dominate, if $x > 1.25$. Soft x-ray emission studies

indicate that the spectra of the crystalline α - and β -phases of Si_3N_4 are similar to each other.¹¹ First-principles electronic structure calculations¹⁰ are in agreement with these results.

Focusing on amorphous hydrogenated silicon nitride am- $\text{SiN}_x\text{:H}$, x-ray photoemission spectroscopy, electron-energy-loss spectroscopy, and optical absorption studies showed that the optical gap opens up once the ratio of Si–Si to N–H bonds falls below 0.10.⁹ The incorporation of hydrogen also causes shift of the Fermi level in $\text{SiN}_x\text{:H}$ by 0.5–0.7 eV toward the CB.⁴ Hydrogen related bonding states are located at 6.3 and 9.8 eV below the VB maximum.⁴ Current-voltage characteristics of charge transport through $\text{SiN}_x\text{:H}$ films suggest to obey small-polaron transport.¹²

Several experimental studies addressed optical properties of SiN_x films. Spectroscopic ellipsometry using conventional and synchrotron-radiation light sources has been used to measure the optical response of SiN_x prepared by different techniques in the energy range from 1.5 to 9.5 eV.¹³ A dual role of H in the fundamental band gap E_g has been noticed: It can cause an increase⁹ and reduction in E_g .¹³ A shift of the optical spectra toward lower energies with increasing the H concentration¹³ has been ascribed to H induced reduction in both band gaps. Soft x-ray studies showed drastic H induced change in the density, network, and surface morphology of SiN_x .¹⁴

Theoretical studies within the framework of density functional theory (DFT) have been employed to study band structure, effective masses, density of states (DOS), charge density, chemical bonding, and optical properties of different polymorphs of cr- Si_3N_4 .¹ Amorphous silicon nitride structures (am- SiN_x and am- $\text{SiN}_x\text{:H}$) have also been studied. Model structures were generated by either molecular dynamics simulations or by a network forming approach.^{7,15–18} While all modeling approaches battle with substantial

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FIG. 1. Schematic presentation of structures for (a) α - and (b) β - Si_3N_4 , (c) am- Si_3N_4 , (d) cr- $\text{Si}_2\text{N}_3\text{H}$, and (e) am- $\text{Si}_2\text{N}_3\text{H}$.

amounts of structural defects in the disordered models, the network approach emerged as the most efficient tool to generate reliable structural models of amorphous SiN_x ,⁵ $\text{SiN}_x\text{:H}$,⁷ and $\text{Si}_2\text{N}_2\text{O}$,¹⁵ with well-defined bond topology.

The results of the modeling studies indicate that stoichiometric am- Si_3N_4 exhibits substantial internal stresses, responsible for the development of topological defects such as dangling (threefold coordinated Si and twofold coordinated N) and floating (fivefold coordinated Si and fourfold coordinated N) bonds. Introducing H and O atoms into the struc-

ture, thus, lowering the average connectivity of the network, then reduces considerably the internal strain in amorphous silicon nitride. Their impact on the electronic structure and optical properties is also drastic. Hydrogenation of a defect-rich disordered structure obviously reduces the concentration of band gap states through termination of dangling bonds.⁸ Even small amount of H affects considerably the electronic structure and optical properties of silicon nitride.^{5,7} While these initial considerations were encouraging, the science around silicon nitride lacks a systematic analysis of influence of structural disorder and impact of hydrogen on the optical properties of silicon nitride.

The aim of this work, therefore, is to perform a comparative analysis of the electronic structure and the optical properties of cr- Si_3N_4 , am- Si_3N_4 , cr- $\text{Si}_2\text{N}_3\text{H}$, and am- $\text{Si}_2\text{N}_3\text{H}$. To anticipate our results, we found that levels close to the fundamental edge are most impacted by structure and chemistry of the amorphous phase. Consequently, control over the latter allows to adjust and finetune the former.

II. METHODS

A. Computational details

The cr and am modifications of Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$ are schematically presented in Fig. 1. Structural data of cr- Si_3N_4 (α - and β - Si_3N_4) and cr- $\text{Si}_2\text{N}_3\text{H}$ were taken from Refs. 19 and 20, respectively (Table I). Models of stoichiometric am- Si_3N_4 and of hydrogenated am- $\text{SiN}_x\text{:H}$ were generated

TABLE I. Primitive unit-cell dimensions, volumes, and structural parameters for cr- and am- Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$. Experimentally determined lattice parameters of Refs. 19 and 20 (in parentheses) have been used as input for *ab initio* studies of cr- Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$, respectively.

Compound	Space group	Unit cell (Å)	Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>
α - Si_3N_4	$P\bar{3}1$	$a=7.808(7.752)$	Si1	6c	0.2535(0.2532)	0.1673(0.1672)	0.4508(0.4509)
		$c=5.660(5.620)$	Si2	6c	0.0825(0.0822)	0.5122(0.5119)	0.6593(0.6580)
		$V=298.81(292.45)$	N1	6c	0.6555(0.6550)	0.6096(0.6111)	0.4322(0.4297)
			N2	6c	0.3143(0.3153)	0.3189(0.3197)	0.6968(0.7006)
			N3	2b	0.3333(0.3333)	0.6667(0.6667)	0.6032(0.5999)
			N4	2a	0.0000(0.0000)	0.0000(0.0000)	0.4513(0.4541)
β - Si_3N_4	$P6_3$	$a=7.572(7.602)$	Si	6h	0.1744(0.1773)	0.7682(0.7677)	0.2500(0.2500)
		$c=2.896(2.907)$	N1	2c	0.3333(0.3333)	0.6667(0.6667)	0.2500(0.2500)
		$V=143.79(145.46)$	N2	6h	0.3303(0.3333)	0.0304(0.0323)	0.2500(0.2500)
am- Si_3N_4	$P1$	$a=11.878$	Si	1a			
		$b=9.994$	N	1a			
		$c=9.629$, $\alpha=85.65$,					
		$\beta=88.55$, $\gamma=95.66$					
		$V=1133.62$					
cr- $\text{Si}_2\text{N}_3\text{H}$	$Cmc2_1$	$a=9.265(9.193)$	Si	8b	0.1744(0.1737)	0.1587(0.1560)	0.0179(0.0000)
		$b=5.456(5.410)$	N1	8b	0.2109(0.2130)	0.8750(0.8630)	0.1684(0.1500)
		$c=4.857(4.819)$	N2	4a	0.5000(0.5000)	0.7581(0.7580)	0.0834(0.0700)
		$V=245.49(239.65)$	H	4a	0.5000(0.5000)	0.0976(0.0968)	0.7185(0.8044)
am- $\text{Si}_2\text{N}_3\text{H}$	$P1$	$a=11.122$	Si	1a			
		$b=10.072$	N	1a			
		$c=12.178$, $\alpha=89.97$,					
		$\beta=84.72$, $\gamma=97.26$					
		$V=1347.51$					

using the network approach together with subsequent *ab initio* molecular dynamics simulations.⁵⁻⁷ The models of am-Si₃N₄ and am-Si₂N₃H consist of 112 and 144 atoms, respectively.

The band-structure calculations have been performed using the Vienna *ab initio* simulation package (VASP),^{21,22} which calculates the Kohn–Sham eigenvalues in the framework of the DFT within the local density approximation (LDA). The exchange and correlation energy of electrons is described through the Perdew–Zunger parametrization²³ of the quantum Monte Carlo results of Ceperley and Alder.²⁴ We use the projector-augmented wave method.^{25,26} Atomic cores are described by pseudopotentials as implemented in the VASP package. The application of the pseudopotentials allows us to construct orthonormalized all-electron-like wave functions for the Si 4s and Si 4p, N 2s and N 2p, and H 1s valence electrons. Spin-orbit coupling was not included in the present calculations.

The imaginary part of the dielectric function $\varepsilon_2(\omega)$ was calculated by the DFT within LDA approximation.^{27,28}

$$\varepsilon_2^{ij}(\omega) = \frac{Ve^2}{2\pi\hbar m^2 \omega^2} \int d^3k \sum_{nn'} \langle kn|p_i|kn'\rangle \langle kn'|p_j|kn\rangle \times f_{kn}(1-f_{kn'})\delta(f_{kn'}-f_{kn}-\hbar\omega). \quad (1)$$

Here $(p_x, p_y, p_z)=p$ is the momentum operator, f_{kn} is the Fermi distribution, and $|kn\rangle$ is the crystal wave function, corresponding to energy ε_{kn} with momentum k . $V/8\pi^3$ is the normalization constant of the integral over reciprocal space. More computational details can be found in Refs. 27 and 28. The trigonal and hexagonal structures of α - and β -Si₃N₄ are optically anisotropic; thus, two components of the dielectric function corresponding to the electric field parallel ($E\parallel c$) and perpendicular ($E\perp c$) to the crystallographic c -axis have been considered. For orthorhombic Si₂N₃H three components of $\varepsilon_2(\omega)$ have been considered. Six components of optical spectra have been calculated for the amorphous structures. In the paper we have presented the results for the direction $E\perp c$. To facilitate the comparison with experimental data,^{25,26} we applied a broadening using a Lorentzian function with a full width at half maximum of 0.002 eV.

The real part of the dielectric function $\varepsilon_1(\omega)$ is then calculated using the Kramers–Kronig transformation. The two dielectric functions were then used to calculate other optical properties. In this paper, we presented the absorption coefficient $\alpha(\omega)$, the reflectivity $R(\omega)$, the refractive index $n(\omega)$, and the extinction coefficient $k_e(\omega)$ calculated using the following expressions:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2, \quad (2)$$

$$\alpha(\omega) = \sqrt{2\omega} \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)}, \quad (3)$$

$$n(\omega) = \sqrt{\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)}{2}}, \quad (4)$$

FIG. 2. Number of bonds per bond length for α - and β -Si₃N₄, am-Si₃N₄, cr-Si₂N₃H, and am-Si₂N₃H.

$$k_e(\omega) = \sqrt{\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)}{2}}. \quad (5)$$

Here $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the complex dielectric function. The optical spectra are calculated by DFT within LDA approximations for the energy range 0–14 eV.

III. RESULTS AND DISCUSSION

A. Bond length distribution

In Fig. 2 we show the Si–N bond length distribution for the crystalline compounds α - and β -Si₃N₄, and cr-Si₂N₃H, as well as for the amorphous structures of am-Si₃N₄ and am-Si₂N₃H. The crystalline structures have well-defined Si–N bond lengths of about 1.73 Å, while the amorphous models show a much broader distribution of Si–N bond lengths, including some pretty long interaction distances up to 2.2 Å. Previous computational studies, however, indicated that a significant medium-range order up to the neighbor shell persists in the amorphous state of Si₃N₄ and Si₂N₃H.^{7,18}

We analyzed the bond coordination in detail for all the silicon nitride structures for distances lengths ≤ 2.0 Å (Table II). α - and β -Si₃N₄ exhibit Si fourfold coordinated by N and N threefold coordinated by Si.^{1,9} The model structure of am-Si₃N₄ comprises one single Si atom in threefold coordination to N, while three Si have five bonds to adjacent N atoms. Two N possess two coordinated bonds, and four N possess four coordinated bonds. In cr-Si₂N₃H [=Si₂N₂(NH)] Si atoms are also fourfold coordinated by N. Two types of N exist, one N threefold coordinated by Si and the other bonded to two Si and one H. The model structure of am-Si₂N₃H comprises all Si fourfold coordinated by N, and in so far resembles the crystalline structure. The detailed coordination of N atoms, however, is more complicated. The majority of N atoms are threefold coordinated to Si. While this resembles the crystal structure as well, some topological defects appear. For both amorphous model structures we observe that topological defects develop primarily at N atoms. Moreover, optimized models of am-Si₃N₄ tend to have an average coordination number for Si and N slightly larger

TABLE II. Number of occurrences of bond coordinations in the unit cells of *cr*- and *am*-Si₃N₄ and Si₂N₃H for atomic distances <2 Å.

Bond coordination	α -Si ₃ N ₄	β -Si ₃ N ₄	<i>am</i> -Si ₃ N ₄	<i>cr</i> -Si ₂ N ₃ H	<i>am</i> -Si ₂ N ₃ H
1
12	6	44	8	48
3
2
16	8	59	8	47
3
2
4	16
6
1

than the crystal structure values of 4 and 3, respectively.²⁹ The above results confirm the validity of the amorphous nature of *am*-Si₃N₄ and *am*-Si₂N₃H.

B. DOS

Figure 3 displays the total DOSs of α - and β -Si₃N₄, *am*-Si₃N₄, *cr*-Si₂N₃H, and *am*-Si₂N₃H in the energy range from -3 to +6 eV. The fundamental band gaps E_g have been determined as the difference of energies corresponding to the VB and CB edges. The magnitude of E_g is equal to 4.6 eV for α -Si₃N₄, 4.2 eV for β -Si₃N₄, ~3.5 eV for *am*-Si₃N₄, 5.0 eV for *cr*-Si₂N₃H, and ~3.4 eV for *am*-Si₂N₃H. The total DOS for *am*-Si₃N₄ and *am*-Si₂N₃H possesses tails in the band gap formed due to lattice disorder and under/overcoordinated structural defects. The calculated band gaps agree well with those of Refs. 1 and 5. However, those for α - and β -Si₃N₄ are smaller than 4.7–4.9 eV determined¹¹ from the analysis of the soft x-ray emission spectra for these two polymorphs. The fundamental band gap of 5.4 eV of *am*-Si₃N₄ determined³⁰ from the energy loss spectra of N 1s photoelectrons is larger than the calculated 3.5 eV. There are no experimental data for both *cr*- and *am*-Si₂N₃H. The experimental results for the band gap of SiN_x:H are available for $x \approx 1.3$, which is in the range 4.5–5.0 eV.⁸ As expected the calculated band gaps are underestimated than the experimentally measured ones due to the well known deficiency of DFT. The band gap for *cr*-Si₂N₃H is much larger than that of

FIG. 3. Total DOS for α -Si₃N₄, β -Si₃N₄, *am*-Si₃N₄, *cr*-Si₂N₃H, and *am*-Si₂N₃H. The Fermi level is set to zero.

α - and β -Si₃N₄. This result is consistent with the experimental and theoretical results regarding H induced widening the band gap.⁹

Insight into the bonding interaction between constituents and the origin of CB and VB electronic energy levels can be obtained from the analysis of the site and orbital projected (PDOS) presented in Fig. 4. The lowest bands located in the energy range from -20 to -14 eV are mainly contributed by

FIG. 4. The orbital and site-projected DOS for α - and β -Si₃N₄, *am*-Si₃N₄, and *am*-Si₂N₃H. The Fermi level is set at zero of energy.

FIG. 5. (Color) Calculated optical spectra for α - and β - Si_3N_4 , am- Si_3N_4 , cr- $\text{Si}_2\text{N}_3\text{H}$, and am- $\text{Si}_2\text{N}_3\text{H}$ along with experimentally measured ones for am- SiN_x grown by spray pyrolysis (Ref. 32) and chemical vapor deposition (Ref. 13). The absorption coefficients are given in cm^{-1} divided by 10^5 .

N 2s electrons with noticeable Si 3p and 3s electrons. The upper part of the VBs located in the energy range from -9 to 0 eV is basically contributed from Si 3p and N 2p states. The bottommost CB of α - and β - Si_3N_4 , am- Si_3N_4 , as well as cr- and am- $\text{Si}_2\text{N}_3\text{H}$ is basically contributed from Si 3p and 3s and N 2s and 2p electrons. These results are consistent with previous theoretical¹ and experimental^{4,31} results.

C. Optical properties

The calculated optical spectra for the α - and β - Si_3N_4 , am- Si_3N_4 , and cr- and am- $\text{Si}_2\text{N}_3\text{H}$ are presented in Fig. 5. The imaginary parts of the optical dielectric response function, absorption coefficient, and reflectivity spectra have been analyzed. Since the crystal structures of the Si_3N_4 phases are hexagonal, the optical spectra of the electric field components perpendicular ($E \perp c$) and parallel ($E \parallel c$) to the c -axis should both be analyzed. Our analysis showed that optical spectra of Si_3N_4 between these two directions are almost the same in the energy ranges from 0 to 8 eV and from 11.5 to 20 eV. So, optical spectra for the direction $E \perp c$ have been analyzed for all the structural modifications of silicon nitride considered in the present paper.

As noted above, the fundamental band gap has been underestimated because of the deficiency of the DFT. Consequently, the calculated optical spectra in Fig. 5 are shifted toward lower energies than the really existing ones. Since the SiN_x and $\text{SiN}_x\text{:H}$ do not contain d electrons included into the valence complex, the band gap underestimation and shift of the optical spectra are not as severe as, say, in ZnO. Often the rigid shift technique is applied to fix partially the band gap problem. The way of correcting the band gap has not been applied here. The calculated optical spectra have been compared with the experimental results for SiN_x prepared by spray pyrolysis³² and chemical vapor deposition.¹³

The analysis of Fig. 5 shows that absorption of am- Si_3N_4 and $-\text{Si}_2\text{N}_3\text{H}$ starts at ~ 4.8 eV, whereas that of cr- Si_3N_4 and

$-\text{Si}_2\text{N}_3\text{H}$ starts from ~ 5.0 eV. The difference in the absorption edge energies shows that band tails of am- Si_3N_4 play an important role in optical transitions. However, both am- and cr- Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$ are transparent in the energy range of photons 0.0 – 4.8 eV. Furthermore, the absorption coefficient and reflectivity are lower than 10^5 cm^{-1} and 0.25 , respectively.

The shift of the fundamental absorption edge of am- Si_3N_4 and $-\text{Si}_2\text{N}_3\text{H}$ toward lower energies compared to their crystalline counterparts is well known to be due to absorption by the tail states located right up the topmost VB and below the bottommost CB of cr- Si_3N_4 . At lower energies of 3 – 7.5 eV the absorption coefficient, reflectivity, refractive index, and the extinction coefficient of am- Si_3N_4 and $-\text{Si}_2\text{N}_3\text{H}$ are larger than those of their crystalline counterparts. However, at higher energies in the range 7.5 – 20 eV the difference is negligible. Since, am- Si_3N_4 and $-\text{Si}_2\text{N}_3\text{H}$ can more easily be formed than their crystalline counterparts, they can be used instead of the crystalline one.

The analysis of Fig. 5 shows that the optical spectra of both cr- and am- Si_3N_4 are shifted toward lower energies compared to those of cr- and am- $\text{Si}_2\text{N}_3\text{H}$. This result is consistent with the experimentally established result regarding the H induced widening of the fundamental band gap.⁹ Although the band gap calculated by DFT has been underestimated and the optical spectra have been shifted to lower energies, they are in good agreement with those for SiN_x prepared by Spray Pyrolysis (SP) and Chemical Vapor Deposition (CVD) techniques (Fig. 5). The reason of the deviation can be related to overestimation of the momentum matrix elements, neglect of the Coulomb interaction between free electrons and holes (excitons), and local-field and finite lifetime effects. Furthermore, in the calculations of the imaginary part of the dielectric response function, only direct optical transitions from occupied to unoccupied states have been considered. For the optical calculations, many more $\mathbf{k}$ points are needed in order to obtain convergence than in the ground-state calculation. Due to memory restrictions of the supercomputers in the present work a number of $\mathbf{k}$ points in the irreducible Brillouin zone have slightly exceeded that used in the ground-state calculation for large supercells of am- Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$. Also, charge fluctuations and the experimental resolution smear out many fine features. These points might be the reasons of the above mentioned deviation between the theory and experiment.

IV. CONCLUSION

Electronic structure and optical properties of am- and cr- Si_3N_4 and $\text{Si}_2\text{N}_3\text{H}$ are studied. Acceptor and donor type bands have been found in the band gap of am- Si_3N_4 and $-\text{Si}_2\text{N}_3\text{H}$ formed by under-/overcoordinated Si and N atoms and lattice disorder. No such bands are found in the fundamental band gap of cr- Si_3N_4 and $-\text{Si}_2\text{N}_3\text{H}$. From orbital and site-projected DOS nature of the VB and CB has been determined. It is shown that the topmost VB mostly consists of Si and N p states. CB minimum of both am- and cr- Si_3N_4 consists of well hybridized Si and N s and p orbitals. We found that optical properties of am- Si_3N_4 and $-\text{Si}_2\text{N}_3\text{H}$ only

slightly differ from those of crystalline counterparts. The difference is found in the energy range close to the fundamental band gap. At larger energies exceeding the fundamental band gap the difference is negligible. Both am- and cr-Si₃N₄ and -Si₂N₃H are found to be transparent in the visible spectra. Thus it can be concluded that the amorphous silicon nitrides can be used instead of their crystalline counterparts for various applications such as antireflection coatings for solar cells, etc., in which optical properties of such materials are important.

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