

Electron energy loss near-edge structures of cubic Si_3N_4

Isao Tanaka^{a)}

Department of Energy Science and Technology, Kyoto University, Yoshida, Sakyo, Kyoto 606-8501, Japan

T. Mizoguchi

Department of Materials Science and Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-8501, Japan

T. Sekine, Hongliang He, K. Kimoto, and T. Kobayashi

National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba 305-0044, Japan

Shang-Di Mo and W. Y. Ching

Department of Physics, University of Missouri-Kansas City, Kansas City, Missouri, 64110-2499

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Electron energy loss near-edge structures of the newly discovered cubic- Si_3N_4 at the Si $L_{2,3}$ edge and N K edge have been measured. The same edges were calculated using a first-principles supercell approach, including the core-hole interaction. The experimental spectra at the two edges were satisfactorily reproduced by the calculations, confirming that the present calculation has sufficient predictive power. The difference in spectral shapes between c - Si_3N_4 and β - Si_3N_4 is more clear for the Si $L_{2,3}$ edge. However, the difference cannot be simply explained by the difference in coordination numbers of Si. © 2001 American Institute of Physics. [DOI: 10.1063/1.1360232]

Cubic silicon nitride (c - Si_3N_4) having spinel structure was discovered by Zerr *et al.*¹ in 1999. Soon after the discovery, Mo *et al.*² reported that c - Si_3N_4 should have a direct band gap of 3.45 eV by means of a first-principles band structure calculation, in contrast to the wider and indirect band gaps of conventional Si_3N_4 with hexagonal form. The existence of the direct band gap implies the potential application of c - Si_3N_4 for light emitting devices, in addition to the use for structural components.

The advantage of the spinel structure resides in the presence of two cation sites. Properties of compounds can be tuned in a wide range by the combination of two cations. The manner to change the electronic states of c - Si_3N_4 by doping or by the formation of double nitrides was first discussed in the binary system Si_3N_4 - Ti_3N_4 by Ching *et al.*³ First-principle calculation of twenty spinel nitrides were then made, in order to survey the properties and stabilities of other potential spinel nitrides.⁴ Detailed calculations of Ge_3N_4 have been reported by two other groups.^{5,6} Despite these predictions, synthesis of spinel nitrides have thus far been succeeded only for Si_3N_4 ^{7,8} and Ge_3N_4 .^{9,10} These compounds were first synthesized using a laser-heated diamond anvil cell. Recently, Sekine *et al.* succeeded in the massive production of c - Si_3N_4 by a shock-compression method,⁷ which broke the bottleneck of sample quantity necessary for detailed investigation of macroscopic properties of the new compounds.

The modern transmission electron microscope (TEM) is often equipped with electron energy loss spectrometer (EELS). Under ordinary experimental conditions of TEM, the near edge structures of EELS (ELNES) is similar to XANES (x-ray absorption near edge structures). In the core-loss process, an electron is excited from a core level to an

unoccupied state by an electric dipole transition. As a result, experimental ELNES is related to unoccupied partial density of states of the selected atom that is allowed by the electric dipole selection rule. Because of the combination with TEM, ELNES can be measured even in a nanometer-sized specimen, when it is embedded in different kind of materials. Therefore it is a useful tool to characterize new materials that are developed by innovative processing. We have often seen that the shape of ELNES in a crystalline phase looks similar to the amorphous phase when their local atomic arrangements are close to each other. ELNES is therefore used as the “fingerprint” of the local structures. However, unless the relationship between “fingerprints” and the local structures is well clarified, information from ELNES cannot be fully utilized. Thus, reliable theoretical calculations with sufficient predictive power prior to detailed experimental investigations are desirable. In this letter, we report the theoretical ELNES with the experimental spectra for c - Si_3N_4 in comparison to β - Si_3N_4 , in order to understand the origin of the spectral features.

c - Si_3N_4 specimens used in the present study were synthesized by a shock-compression method that has been described elsewhere.⁷ The β - Si_3N_4 sample was a commercially available one. A TEM with a field-emission electron gun (Hitachi, HF-3000) was operated at an accelerating voltage of 300 kV. A parallel detection electron energy-loss spectrometer (Gatan, Digi-PEELS) was also used. All spectra were measured with a dispersion of 0.1 eV per channel. The full width at half maximum of the zero-loss peak, that is a measure of the energy resolution, was 0.7 eV. The exposure times were 5 and 20 s for Si L and N K edges, respectively. To avoid the dynamical diffraction effect, the measurements were performed excluding exact Bragg conditions.

Theoretical calculations of ELNES were made using the density-functional theory based first principles orthogonal-

^{a)}Electronic mail: itanaka@MTL.kyoto-u.ac.jp

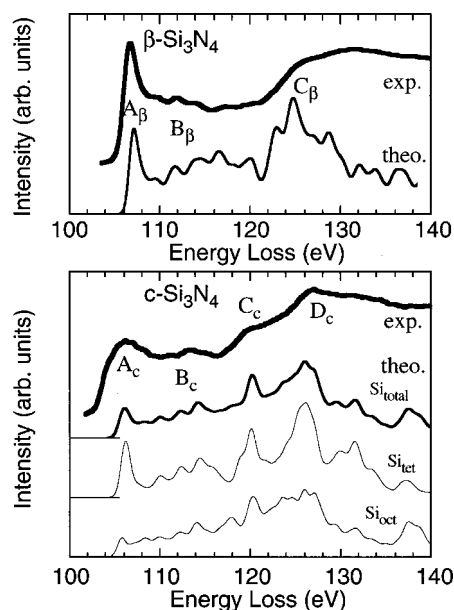


FIG. 1. Experimental Si $L_{2,3}$ edge ELNES (exp.) from β - and c - Si_3N_4 in comparison with theoretical spectra (theo.).

ized linear combination of atomic orbitals (OLCAO) method, using a supercell composed of 112 atoms. To achieve high resolution, 27 k points in the total Brillouin zone of the supercell were used for the k -space integration. In order to reproduce the experimental ELNES satisfactorily, inclusion of the core-hole relaxation effect at the final state of the electronic transition is mandatory. A rigorous scheme to include the core-hole effects has been implemented in the OLCAO method, as described elsewhere.¹¹ Transition energy (energy loss) was obtained as the difference in total energies from two separate supercell calculations: The initial ground state, and the final state with the presence of a core-hole.

The experimental spectra at the Si $L_{2,3}$ edge are compared with the theoretical spectra in Fig. 1. Experimental ELNES of β - Si_3N_4 can be decomposed into three features, i.e., a sharp peak A_β , a set of small humps, B_β , and a large and broad peak C_β for convenience. These peaks are well reproduced by the calculation, except for the higher energy region above 130 eV.¹² The fine structures in B_β are also in agreement. The sharpness of the peak A_β is not seen in the partial density of states at the ground states.¹³ The strong intensity can be ascribed to the presence of the Si $2p$ core-hole, which brings about the localization of the wave function responsible for the peak A_β , as has been pointed out in a number of works.^{11,14–16}

The experimental spectrum from c - Si_3N_4 is remarkably different from that of the β - Si_3N_4 . The theoretical spectra were obtained for two Si sites in c - Si_3N_4 , i.e., Si_{tet} (tetrahedral site) and Si_{oct} (octahedral site), by two separate calculations. They were combined with a double weighting to Si_{oct} . The experimental spectra can be decomposed into four features, denoted as A_c to D_c . There are smaller features in the experimental spectra that can not be clearly resolved. The four features are reproduced by the theoretical spectrum. The apparent differences between two phases are twofold: (1) The first peak, $A_{c/\beta}$, is smaller and broader in c - Si_3N_4 , and (2) A peak at around 120 eV can be found only in c - Si_3N_4 as

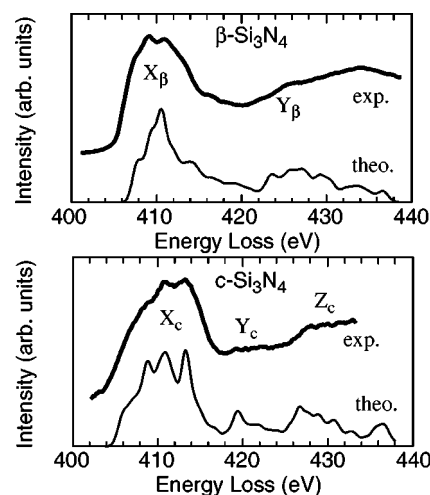


FIG. 2. Experimental N K edge ELNES from two Si_3N_4 in comparison with theoretical spectra.

denoted by C_c . Similar to the case of peak A_β , peak A_c does not appear in the density of states at the ground state.² In other words, the strong core-hole interaction makes the peak. The broadening of the peak A_c , in the theoretical spectrum can be mainly ascribed to the difference in the peak positions between Si_{tet} and Si_{oct} by 0.4 eV.¹⁷ This difference is already apparent in the Si $2p$ core level energies of the two Si sites, in the initial ground state calculation. Other than the small shift in the peak A_c , all peaks are more distinctive for Si_{tet} , and show the differences in the intensity of various peaks.

The cation $L_{2,3}$ edge spectra have sometimes been interpreted with respect to their coordination numbers. Brydson *et al.* made a multiple scattering calculation for Al octahedrally and tetrahedrally coordinated to a single shell of oxygen atoms.¹⁸ They used the results to interpret the Al $L_{2,3}$ edge spectrum from a complex mineral. Bruley used the result to evaluate the degree of disordering in spinel- MgAl_2O_4 ,¹⁹ and also to interpret the spatially resolved ELNES from a grain boundary of Al_2O_3 .²⁰ Clearly, the idea that tetrahedrally and octahedrally coordinated cations have different fingerprints is oversimplified, and does not work well for the c - Si_3N_4 . The present calculation shows that the spectra cannot be interpreted in such a simple manner. One may easily be led to the wrong conclusion that the spectrum from β - Si_3N_4 can be used as a “finger print” for Si_{tet} in c - Si_3N_4 .

Figure 2 shows experimental and theoretical N K edge ELNES.²¹ Two features in β - Si_3N_4 and three features in c - Si_3N_4 are satisfactorily reproduced. When two experimental spectra are compared, the difference in spectral shape is less clear for the N K edge than the Si $L_{2,3}$ edge. However, the shape of the first broad peak, $X_{c/\beta}$, is quite different between two phases. The first peak of the spectrum from c - Si_3N_4 can be decomposed into several peaks. The present theoretical calculation has been successful in reproducing these fine structures.

Although the present calculations satisfactorily reproduce the experimental spectra at the two edges, it is conceivable that the agreement between theory and experiment may be further improved by considering an even larger supercell, inclusion of spin-orbit coupling in the Si $2p$ core, and inclu-

sion of any other many electron effects beyond the core-hole interaction.

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