

Experimental and Theoretical Evidence for the Covalent Bonding and Charge Transfer in α -Silicon Nitride, A Synchrotron Diffraction Study

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Introduction

Silicon nitride (Si_3N_4) continues to attract many researchers because of interesting mechanical and dielectric properties. The purpose of this work is to study the electron-density distribution of α - Si_3N_4 using synchrotron powder diffraction data. Density functional theory (DFT) is employed to calculate the electron density distribution and elastic properties. The covalent bonding between the Si and N atoms is observed in the experimental electron-density distribution of α - Si_3N_4 for the first time in the present study (Yashima *et al.*, *J. Phys. Chem. B*, **111**, 3609 (2007)).

Experiments

Synchrotron x-ray powder diffraction experiments of a commercial silicon nitride material were performed at 299 K using the multiple-detector system installed at the BL-4B₂ beam line of the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. A monochromatized 1.20490(1) Å x-ray beam was utilized. The crystal structures of the silicon nitrides were refined by the Rietveld method with a computer program RIETAN-2000 (Izumi & Ikeda, 2000). Electron-density distribution of α - Si_3N_4 was investigated by a maximum-entropy method (MEM, PRIMA (Izumi & Dilanian, 2002)) and DFT calculations.

Results and discussion

All the reflection peaks in the synchrotron powder diffraction pattern of the present silicon nitride powders were indexed by the α - and β - Si_3N_4 phases. Space groups $P31c$ and $P6_3/m$ were assumed for the α - and β - Si_3N_4 , respectively. Weight fractions of α - and β - Si_3N_4 calculated using the refined crystallographic parameters and scale factors were 0.975 and 0.025, respectively. In combination with density functional theory (DFT) calculations, the present experimental electron-density distribution of the α - Si_3N_4 indicates covalent bonds between Si and N atoms and the charge transfer from the Si to N atom (Fig. 1). The MEM experimental electron density is consistent with the theoretical DFT valence electron density. The triangular distribution around N atoms was found in both experimental and theoretical

electron density distributions, which is attributable to the nitrogen sp^2 hybridization for the nearest silicon and nitrogen pairs. The minimum electron density in an intralayer Si-N bond was a little lower than that in an interlayer bond, which would be responsible for the inequality between elastic constants $C_{33} > C_{11}$. The present work suggests that the high bulk modulus of the α - Si_3N_4 is attributable to the high minimum electron density of the Si-N bond.

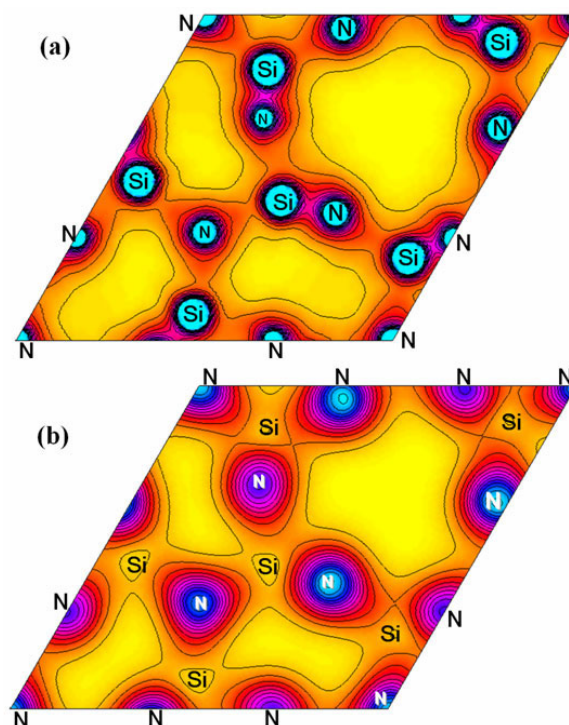


Fig.1. Projected MEM and valence electron density distributions in α - Si_3N_4 ($0.3 < z < 0.7$) obtained through (a) MEM analysis of synchrotron diffraction data and (b) DFT calculations, respectively. Contour lines from 6 to $40 e\text{\AA}^{-3}$ by the step of $5 e\text{\AA}^{-3}$.

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