Electronic Structures of TiN and TiC ——Extension of Molecular Orbital Method into Crystals

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Density of states and theoretical X-ray emission spectra for the valence bands of TiN and TiC are obtained with a molecular orbital method. To describe electronic structures of crystals, local clusters for the molecular orbital calculations are extended, including the effects from the outside of the cluster in the crystal. The theoretical results are in good agreement with the experimental ones.

Keywords : molecular orbital/ TiN/ TiC/ electronic structure/ extended cluster model/ X-ray emission spectra

X-ray spectroscopy is one of the most powerful tools for elucidating electronic structures of substances. Valence band structures are studied with X-ray photo-electron spectra (XPS) and X-ray emission spectra (XES). XPS reflects density of states (DOS), while XES reflects partial density of state. According to the dipole selection rule on the radiative transition, K X-ray emission reflects p components and L_3 X-ray emission corresponds to s and d components. Therefore, detailed valence band structures are clarified by observing both spectra.

Fischer provided a diagram suitable to understand the relation among the X-ray emission spectra for various inner shell excitations[1]. The molecular orbital levels were shown to explain this relation. However, his and the followers' model clusters used to represent solids in the molecular orbital framework were insufficient to make direct and quantitative comparison with the experimental results.

Molecular orbital methods provide an atomic view of materials and are, therefore, useful to get valuable insight about understanding electronic structures and designing materials. They can be also applied to widely extended systems such as solid states.

XES for TiN and TiC have been discussed with cluster calculations though the theoretical spectra were not satisfactory. The simplest TiX_6^{n-} (X=C or N) model cluster is still used to interpret the origins of the peaks in XES. Gubanov et al. [2] interpreted the XES spectra of these compounds with molecular orbital calculations. But in the Ti L_3 spectrum for TiN, the calculated peak intensity ratios were strikingly different from the experimental ones. His theoretical spectra could not explain bands at

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Scope of Research
In order to obtain fundamental information on the property and structure of materials, the electronic states of atoms and molecules are investigated in detail using X-ray, SR, ion beam from accelerator and nuclear radiation from radioisotopes. Theoretical analysis of the electronic states and development of new radiation detectors are also performed.

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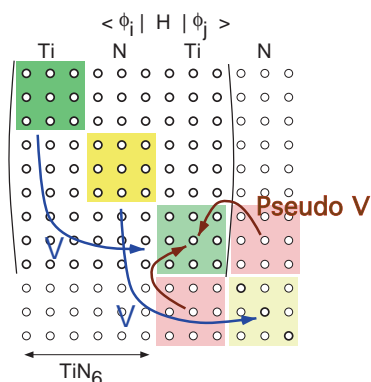NAKANISHI, Yoshikazu (RF)
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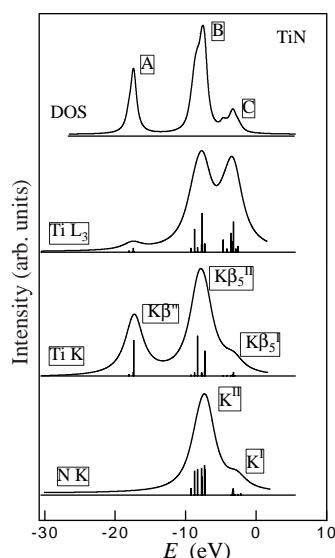**Figure 1.** Energy matrix for a cluster extended to include the environment.

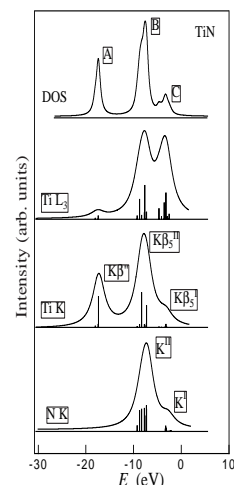
Figure 2. Theoretical DOS and XES for TiN.

Figure 3. Experimental photoelectron spectra [3], Ti L_3, Ti K and N K XES [4] for TiN.

high energy parts of the spectra. He stated that the discrepancies of the uppermost bands for TiN could arise from defect structures in the crystal.

The simple TiX_6^{n-} cluster has a sudden change of bonding environment at the periphery and causes peculiar charge distribution different from the actual crystal. In the present work, to provide theoretical spectra of high quality, an extended cluster model is developed. These clusters can improve the periphery of clusters and the electroneutrality in the stoichiometric composition of crystals. Furthermore, to make a precise comparison, Ti L_3 XES for TiN and TiC are measured, using the synchrotron radiation.

We take a way that the environment around the cluster is involved in the energy matrix for the cluster. Explanation of this matrix is shown in Fig. 1, where the matrix elements for a cluster include the contributions from outside of the cluster in the crystal. The cluster is embedded in ambient potentials which are duplicated from the potentials of the central atoms. Pseudopotentials are placed upon these potentials so that the wave functions of the embedded cluster feel the exclusive character of the wave functions of the ambient atoms. The electro-neutrality of the Ti-X stoichiometric pair is achieved by varying the depth of the pseudopotentials. This procedure reduces the change of the chemical potential of electrons at the ends of the embedded cluster. The electroneutrality is the postulate in this method to connect the cluster smoothly to the environment.

X-ray emission probability was obtained in the dipole approximation. Intensities for three kinds of the Ti atoms in the cluster were summed up to evaluate all the forms of the wavefunctions in the cluster. This summation corresponds to collecting the different momenta of the wavefunctions. To generate the theoretical spectra, a Lorentzian curve was placed at each eigenenergy.

The theoretical DOS and XES obtained are compared with the experimental spectra and the relation among the spectra is illustrated. The theoretical valence

DOS and XES for TiN are plotted in Fig. 2 and the experimental spectra are in Fig. 3. The spectra for TiC are not shown here for the limit of space. The experimental spectra were arranged, referring to the ionization energies of the corresponding initial levels of the excitations. This means the ionization energy for the valence band is plotted for the experimental spectra. Consequently, we have arranged the different XES on the same ground.

For TiN, the theoretical XES in Fig. 2 agree well in shape and position with the experimental spectra of the Ti L_3, Ti K and N K XES shown in Fig. 3. The present theoretical spectra have the uppermost peaks marked with $K\beta_5^{I}$ and K^{I} in the Ti K and N K XES, which could not be explained with the simplest cluster TiX_6^{n-} calculations. The calculated peak intensities for Ti L_3, Ti K and N K are also in good agreement with the corresponding experimental ones.

Our original papers[5,6] present details of valence electronic structures and covalent interaction between the metal and non-metal atoms for TiN, TiC and TiO_2.

References

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