# X-ray photoelectron spectrum and band structure of TiC

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The energy distribution curve of the valence band of a TiC single crystal was measured by x-ray photoelectron spectroscopy (XPS). The XPS measurement supports the augmented plane wave (APW) calculation after Ern and Switendick rather than the semi-self-consistent APW calculation after Conklin and Silversmith. The present modified APW calculation based on the neutral-atomic-charge densities was in good agreement with the XPS measurement. Moreover, the calculation was consistent with such available experimental data as x-ray emission and absorption spectra, optical reflectivity, and low-temperature specific heat. The peak (I) arising from the C 2s state is isolated from the valence-band peak (II) attributed to the C 2p, Ti 3d, and 4s states. The experimental intergrated intensity ratio of peak II to peak I is 2.9 to 1.0 which is nearly equal to the theoretical value 3 to 1. The calculated density of states at the Fermi level is 0.22 electrons/(eV primitive cell), which is nearly equal to the value of 0.23 from the electronic specific heat.

### I. INTRODUCTION

The transition-metal carbides have been studied intensively because of their many interesting properties among which are metallic conductivity, extremely high melting point, extreme hardness, and superconductivity. The combination of these unique properties with very simple atomic structure of rock-salt type makes them particularly attractive for theoretical investigations. Facecentered cubic TiC is the most typical refractory material among such carbides, nitrides, and oxides of group IVb and Vb as ZrC, NbN, TiO, etc. TiC has been most intensively studied among them for the interpretation of the origin of their unique properties. These properties closely connected with the electronic band structure. A lot of information concerned with the band structure of TiC has been obtained from both theoretical and experimental points of view. The mutual agreement among these data, however, is not sufficient to draw definite conclusions about the density of states (DOS) of TiC.

The band structure of TiC has been calculated by several methods<sup>1-5</sup>; the semiempirical tightbinding method by Lye and Logothetis, <sup>3</sup> the augmented-plane-wave (APW) method by Ern and Switendick, <sup>4</sup> and the semi-self-consistent as well as non-self-consistent APW method by Conklin and Silversmith. <sup>5</sup> These calculations have not given the same results. The import differences between the APW calculations and the tight-binding one are in the DOS and the direction of the charge transfer.

As for the charge transfer, the x-ray photoelectron spectroscopic measurements<sup>6, 7</sup> have confirmed the result of the APW calculations which predict the electron transfer from titanium to carbon. However, the tight-binding method by Lye *et al.* predicting the reverse direction in electron transfer is not supported. The amounts of the charge transfer from titanium to carbon are estimated at about 0.2 electrons from the core-level energy shifts of x-ray photoelectron spectroscopic measurement by using the theory based on a free-ion model<sup>§</sup> This small amount of transferred charge infers a weak ionic character of the Ti-C bond.

The experimental data related to the band structure of TiC are x-ray emission and absorption spectra, 9-11 optical reflectivity, 3 low-temperature specific heat,<sup>2</sup> etc. All these data do not, however, support only one of the calculated DOS's. The shape of the Ti K emission band after Ramqvist et al.<sup>9</sup> is consistent with the DOS from the APW calculations but not with the semiempirical tightbinding calculation based on the optical reflectivity. The other Ti  $L_{II,III}$  and C K emission spectra of TiC,<sup>10, 11</sup> however, cannot be used to verify the results of the APW calculations owing to the influence of the selection rule and self-absorption. The DOS at the Fermi level obtained by the lowtemperature specific-heat measurement is smaller than the results from the APW calculations by about a factor of 2 and far smaller than that from the tight-binding method.

Although the APW calculations give relatively reasonable results consistent with such experimental data as the Ti K emission spectrum and the direction of charge transfer, some discrepancies remain between these APW calculations. For example, a peak just below the Fermi level in the histogram of the DOS from the semi-self-consistent APW calculation does not appear in the nonself-consistent APW calculation using a crystal potential based on the superposition of neutralatomic-charge densities. The band structure from the semi-self-consistent APW calculation corresponds to that from the non-self-consistent one using a crystal potential based on the superposition of charge densities from doubly ionized Ti  $(4s^0)^{2+}$  and C  $(2p^4)^{2-5}$  These values of ionic charge seem to be too large for TiC contrary to the experi-

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FIG. 1. X-ray photoelectron spectrum of the valence band of TiC. Dashed line shows a background.

mental result of charge transfer.<sup>8</sup> The Ti K emission spectrum supports the APW calculations but, owing to the limit of resolution, cannot be used to make clear which APW calculation, semi-self-consistent or non-self-consistent, gives a more reasonable DOS.

Therefore it is necessary to study the DOS of TiC in greater detail from both experimental and theoretical sides to make the electronic structure clear. One of the most promising experimental techniques for the investigation of the DOS would be photoelectron spectroscopy using monochromatized x-ray (XPS).<sup>12, 13</sup> The XPS data seem to be very useful for the case where the assumptions of the constant transition matrix element, the freeelectron approximation for the final states, a low contribution of inelastically scattered electrons, and a nearly energy-independent escape depth are relatively reasonable in the explanation of XPS electron processes.<sup>12</sup>

The valence-band spectrum of a TiC single crystal was obtained from a XPS measurement and compared with the DOS from the above-mentioned band calculations. The agreement of the experiment with the non-self-consistent APW calculation was better than with the semi-self-consistent one but was not fully satisfactory. Then some modified APW calculations were performed in several ways by varying the crystal potential, and especially the conduction band was calculated for the 20eV-wide range above the Fermi level. The experimental energy distribution curve (EDC) was in good agreement with the present calculation obtained by using the Slater exchange potential and considering 202 neighbor atoms, which was, moreover, consistent with the x-ray emission and absorption spectra and the low-temperature specific heat. Futhermore it was possible to derive the imaginary part of the complex dielectric constant consistent with that obtained from the optical reflectivity after Lye et al.<sup>3</sup>

In Sec. II of this paper, the measurement of the XPS spectrum and the results are described. In Sec. III, the band structure of TiC obtained by a modified APW calculation is described. In Sec.

IV, the resulting band structure is considered in relation to the experimental works. The conclusions are summarized in Sec. V.

# II. EXPERIMENT AND RESULTS

The TiC single crystal was prepared by the rf floating-zone technique.<sup>14</sup> The ratio of C to Ti of the crystal determined by an electron microprobe x-ray analyzer was 0.98. The specimen of TiC was lapped with alumina powder and sequentially diamond paste, and last polished with emery paper in an Ar-gas atmosphere. Then the sample was inserted into the analyzing chamber without exposing to the air. The measurement was performed on an HP 5950A ESCA spectrometer with a resolution of 0.7 eV. The pressure in the analyzing chamber was  $5 \times 10^{-9}$  Torr, which was measured with a nude-type Bayard-Alpert gauge. The sample was heated at a temperature of 300 °C during the measurement with the aim of the cleaning of the surface. It was verified from the EDC after Ar-ion etching and heating treatments that the contribution of surface contaminants to the EDC in the region of the valence band was of the level of a broad background. Although small peaks from surface contaminants such as the C 1s peak corresponding to hydrocarbons and the O 1s peak were detected even when great care was exercised, the Ti 2p peak corresponding to titanium oxide was not observed.7

Figure 1 reproduces the experimental valenceband spectum of TiC without any correction. It took the elapsed time of 39 h. The Fermi level was determined from the Fermi edge in the spectrum of platinum. It was confirmed that the shift of the leading edge of the valence band due to the charging effect was not observed for the TiC sample by using the electron flood gun technique. A dotted line in the figure shows a backgound from



FIG. 2. Corrected x-ray photoelectron spectrum (a) compared with the theoretical density-of-states histograms (b) by Ern and Switendick (Ref. 4) and (c) by Conklin and Silversmith (Ref. 5).

inelastically scattered electrons which is proportional to the spectrum intensity integrated from the Fermi level to the considered point. The corrected XPS spectrum in Fig. 2 (a) was obtained by subtracting the backgound from the experimental curve. Two large peaks appear in this spectrum. The position and the full width at half-maximum (FWHM) of the peak marked II on the lower binding energy side are 3.4 and 3.7 eV, respectively, and those of the peak I are 10.7 and 3.2 eV. The type of the distribution function of both peaks is shaped like a Lorentzian, while the shape of the EDC of platinum at the Fermi edge is an intermediate type between a Lorentzian and a Gaussian. The ratio of the peak II to the peak I in the integrated intensity is 5.8 to 2.0, which is nearly equal to the ratio of six electrons from Ti  $3d^2$ ,  $4s^2$ , and C  $2p^2$  to two from C  $2s^2$ . The ratio was observed to decrease a little in the presence of hydrocarbon surface contaminants.

The XPS spectrum suggests that the APW method is more successful in the determination of the DOS of TiC than the semiempirical tight-binding method.<sup>3</sup> The DOS from the tight-binding calculation is largely different from the XPS EDC, particularly in regard to the DOS at the Fermi level and the position of the peak derived from the C 2s state. Figures 2 (b) and 2 (c) show the DOS histograms of TiC calculated from the APW method.<sup>4,5</sup> The histogram in Fig. 2 (b) was obtained from the non-self-consistent (NSC) calculation by Ern et al. by using the crystal potential based on the superposition of the neutral atomic charge densities and considering 26 neighbor atoms.<sup>4</sup> On the other hand, the histogram in Fig. 2 (c) was obtained from the semi-self-consistent (SC) one by Conklin et al. by using the crystal potential based on an approximately self-consistent charge distribution.<sup>5</sup> The band stucture was calculated on a grid of 32 points in  $\frac{1}{48}$  of the Brillouin zone for both the NSC and SC histograms, and the values of the DOS were determined at an energy interval of 0.075 and 0.05 Ry, respectively.

Figure 2 shows that the agreement between the semi-self-consistent APW calculation and the XPS measurement is not so good. The NSC histogram is in better agreement with the experimental EDC in regard to the outline of the spectrum than the SC histogram is. However, some differences remain between the NSC histogram and the XPS spectrum in the points of peak position and peak width. Both peaks in the NSC histogram are located at lower binding energy than in the XPS EDC by about 1.0 eV. The FWHM's of the peak I and II in the NSC histogram are half as much as those of the experiment. Thus we were inclined to perform all over again the band calculation of TiC in order to obtain a more correct theoretical EDC fit to the XPS one.

#### **III. BAND STRUCTURE AND DENSITY OF STATES**

The APW calculation seems to be the most promising way to arrive at the correct theoretical EDC of TiC, so that some modified APW approaches should be performed. This method requires no empirical assumption, in principle, except the material composition and crystal structure.<sup>15,16</sup> The calculation results, however, depend on the muffin-tin crystal potential being related to the electronic configuration of the constituent atoms, the choice of the exchange potential, the number of neighbor atoms considered, the constant part of the potential, etc. The present calculations were performed by using the Slater exchange potential. or the Kohn-Sham one, and considering a sufficient number of neighbor atoms up to the 14th neighbors. The potentials of the constituent atoms were obtained from the neutral-atomiccharge densites with the program of Herman and Skillman.<sup>17</sup> The computational procedure used in this work is similar to that described by Ern et al.<sup>4</sup> The relevant potential parameters are listed in Table I. The convergence of the eigenvalues were within 0.01 Ry. The energy-band structure was calculated on a grid of 222 points in  $\frac{1}{48}$  of the Brillouin zone.

The band structure and the DOS of TiC are shown in Fig. 3. These results were obtained by using the Slater exchange potential and considering 202 neighbor atoms. Band 1 (being numbered from the lowest-energy side) arising from the C 2s state is separated more than 4.0 eV from the higher band. This band forms an isolated peak marked with I at the energy of 1.0 eV in the DOS. This fact infers that the carbon atom does not form the  $sp^3$  hybrid orbitals, and the C 2s state makes few contribution to the bonding of the C and Ti atoms. The points of  $\Gamma_1$  and  $L_1$  of this band correspond to the lower edge and the upper edge of this peak, respectively. The flat part of this band from  $X_1$  to  $K_1$  over the surface of the Brillouin zone gives rise to the top of the peak.

The three bands 2 to 4 degenerate at the  $\Gamma_{15}$  point arise mainly from the C 2*p* state and partially from the Ti 3*d*. The upper three bands 5 to 7 degenerate at  $\Gamma_{25}^{\prime}$  and the two bands 8 to 9 de-

TABLE I. Lattice constant, APW sphere radius, and constant part of the potential used in the band calculation of TiC in atomic units (1 a.u. = 0.529 Å, 1 Ry=13.605 eV).

$a$ (a. u.) $R_s$ (a. u.) $V_c$ (f      8, 1801    C: 1, 6487: Ti: 2, 3396    -1, 9			
8,1801 C: 1,6487: Ti: 2,3396 -1,9	a (a.u.)	$R_s$ (a.u.)	<i>V<sub>c</sub></i> (Ry)
	8.1801	C: 1.6487; Ti: 2.3396	-1.9061



FIG. 3. Band structure (a) and the density of states (b) of TiC.

generate at  $\Gamma_{12}$  arise from the Ti 3d state. The band 5 from the Ti 3d state goes down from the  $\Gamma'_{25}$  point along the symmetry line  $\Delta$  and overlaps with the band 4 from the C 2p state between the  $\Gamma$  and X points. The mixture of the C 2p and Ti 3d states forms the large peak II below the Fermi level  $(E_{F})$ . These facts mean a large contribution of covalent bond between the C 2p and Ti 3d states to the cohesive energy of TiC. The top of the peak II corresponds to the near degeneracy of the bands 3 and 4 around the symmetry points L and W on the Brillouin zone. A small peak  $(S_{11})$  associated with the peak II corresponds to the flat part from  $\Delta_{\min}$  point to  $\Sigma_{\min}$  of the band 2. The lowest point  $L'_2$  of the band 2 corresponds to the bottom of the peak II. The Fermi level intercepts the four bands 2 to 5 derived from the C 2p and Ti 3d states. The slope of these bands at the Fermi level is relatively sharp and only band 5 exists between the energy levels of the  $\Gamma_{15}$  and  $\Gamma'_{25}$  points. That causes the small DOS of 0.22 electrons/(eV primitive cell) at the Fermi level and the miminum of the DOS just a little above that point. The five bands 5 to 9 mainly derived from the Ti 3d state form the peak III around 16 eV and the flat part of the band 9 from the X point to the K corresponds to a sharp shoulder peak  $(S_{III})$  associated with this peak.

The Ti 4s state contributes to the band 10 at  $\Gamma_1$  point which lies above the Fermi level, so that

the electronic charge in this state is forced to diffuse to the Ti 3d and C 2p states. Therefore the charge transfer from titanium to carbon occurs in TiC compound, and an ionic bond contributes partially to the cohesive energy. The band 10 fills up the valley between the peak III and IV. The upper band 11 arises from the C 3s state. The broad peak IV consists of this band and a fraction of the bands 10, 12, and 13. The three bands 12 to 14 are attributable to the Ti 4p state, which relate to the peak V.

The present band structure has a close resemblance to the result obtained from the assumed neutral atomic charges by Conklin *et al.*<sup>5</sup> However, it has some differences from the result obtained by Ern *et al.*<sup>4</sup> in the relative position and the shape of the bands arised from the C 2p and Ti 3d states, especially at the  $\Gamma_{15}$ ,  $\Gamma_{25}'$ , and  $\Gamma_{12}$  points.

### IV. COMPARISON BETWEEN EXPERIMENT AND CALCULATION

The theoretical EDC was obtained from the present DOS by assuming a Lorentzian smearing function with FWHM of 0.7 eV. Figure 4 (a) shows the close resemblance of this spectrum (dashed line) with the corrected XPS EDC (solid line). The characteristic features of the theoretical EDC can be related to the corresponding features of the experimental one. The binding energy and the FWHM's of the two peaks marked with I and II are listed in Table II for comparison between the theory and the experiment. The energy of the peak I derived from the C 2s state coincides in the both spectra within 0.2 eV. The peak II from the C 2p, Ti 3d and 4s states lies at the same energy within 0.5 eV, and its peak width is nearly equal in both spectra.

The feature of the theoretical EDC at the Fermi



FIG. 4. Comparison of the experimental energy distribution curves of the valence band with the theoretical ones. Solid line—the corrected x-ray photoelectron spectrum (a). Dashed lines—the calculated energy distribution curves using a Lorentzian function with the width of 0.7 (a) and 1.2 eV (b). Dotted line—the corrected x-ray emission spectrum by Ramqvist *et al.* (Ref. 9) (b).

	Binding energy (eV)		Full width at half-maximum (eV)		Ratio of the integrated intensity of peak II	DOS at the Fermi level electrons
	Peak I	Peak II	Peak I	Peak II	to peak I	(eV primitive cell)
Exper.	10.7	3.4	3.2	3.7	2.9:1.0	· ·
Theoret.	10.6	2.9	1.4	3.4	3:1	0.22

TABLE II. The comparison of the experimental EDC with the theoretical one.

level is shaped like the experimental one. The shoulder at the Fermi level which appears in the theoretical EDC is also observed in the XPS spectrum. The DOS of 0.22 electrons/(eV primitive cell) at the Fermi level from the calculation is nearly equal to 0.23 from the low-temperature specific heat<sup>2</sup> but smaller than 0.49 from the magnetic susceptibility.<sup>2</sup> These results and the band structure indicate that TiC is a metal and not a semiconductor, although electrical properties at high temperature have been considered to suggest that TiC can be classified as semiconductor.<sup>18</sup>

Figure 4 (b) shows the theoretical EDC (dashed line) obtained from the present DOS by using a Lorentzian smearing function with FWHM of 1.2 eV. This spectrum is in good agreement with the Ti K emission spectrum (dotted line) obtained by Ramqvist *et al.*,<sup>9</sup> except the position of the top of the peak II. This x-ray emission spectrum has also a close resemblance to the XPS spectrum. It is noteworthy, however, that the shoulder which appeared at the Fermi level in Fig. 4 (a) can not be observed in both spectra smeared with a Lorentzian function with a width of 1.2 eV.

Figure 5 shows the theoretical EDC of the conduction band smeared with the Lorentzian with the width of 1.2 eV (solid line) and the Ti K absorption spectra for  $TiC_{1.0}$  (dashed line) and  $TiC_{0.7}$  (dotted line) observed by Ramqvist et al.<sup>9</sup> The characteristic features in the x-ray absorption spectra can be related to the corresponding ones of the DOS of the conduction band. The peak III on the lowerenergy side corresponds to the transition concerned with the five bands 5 to 9 derived from partially empty Ti 3d state. Peak IV which appears in the spectrum of  $\mathrm{TiC}_{0.7}$  is attributable to band 10 from the Ti 4s state and band 11 from C 3s and partially to band 12 from Ti 4p. Peak V with a large background can be related to the higher-energy bands 12 to 14 from the Ti 4p state. The disagreement of the relative intensity of each peak between the DOS and the x-ray absorption spectra may be caused by the selection rule of the transition.

The imaginary part of the complex dielectric constant ( $\epsilon_2$ ) of TiC was derived from the present

band structure by assuming a constant transition matrix element. Figure 6 shows both theoretical  $\epsilon_2$  curves obtained by assuming direct transition (solid line) or indirect transition (dashed line). The experimental curve (dotted line) was obtained from the Kramers-Kronig (KK) analysis of the reflectivity spectrum by Lye et al.<sup>3</sup> The theoretical  $\epsilon$ , spectrum with the assumption of direct transitions is in fairly good agreement with the experimental one except for a spurious small peak at 4.5 eV which may be eliminated by considering strictly the wave-vector dependence of the matrix element, because this peak must be attributed to the transition between the d-like bands owing to the assumption of the constant matrix element. The energies of the four main peaks marked with  $P_{I}, P_{II}, P_{III}$ , and  $P_{IV}$  are listed in Table III for comparison. The  $P_{I}$  and  $P_{II}$  are associated with the transition between the band 3 or 4 arised from the C 2p and the bands 5 to 7 from the Ti  $d_{\epsilon}$  state. Peak  $P_{III}$  is attributed to the transition between band 2 (C 2p) and bands 5 to 7 (Ti 3d), or the transition between bands 3 to 4 (C 2p) and bands 8 to 9 from the Ti  $d_{\gamma}$  state. Peak  $P_{IV}$  corresponds to the transition between band 1 (C 2s) and bands 5 to 8 (Ti 3d), or the transition between bands 2 to 4 (C 2p) and bands 10 (Ti 4s) and 11 (C 3s).

The present calculation gives the theoretical  $\epsilon_2$  being consistent with the experimental one obtained by the *KK* analysis of the reflectivity. How-



FIG. 5. Comparison of the theoretical energy distribution curves of the conduction band (solid line) with the x-ray absorption spectra for  $\text{TiC}_{1,0}$  (dashed line) and  $\text{TiC}_{0,7}$  (dotted line) by Ramqvist *et al.* (Ref. 9).





ever, the present DOS is far different from the result of the semiempirical tight-binding calculation based on the reflectivity data. This may imply that the tight-binding method is not suitable for the calculation of the band structure of TiC.

A little disagreement between the present theoretical EDC and the XPS one remains in the position of the peak II (Fig. 4). Some approaches to increase the binding energy of the peak II were performed by modifying the crystal potential. Although it may be expected that the binding energy of the valence band increases by underestimating the contribution of the exchange potential.<sup>19</sup> the agreement of the DOS obtained by using the Kohn-Sham exchange potential<sup>20</sup> with the XPS EDC is not better than that by using the Slater exchange potential, as seen in Fig. 7. In this case the binding energy of the peak II does not change while the binding energy of the peak I decreases by 0.5 eV and the width of the valence band corresponding to peak II broadens. On the other hand, the FWHM of peak I of the XPS EDC is larger

TABLE III. Energy of the characteristic features of the theoretical imaginary part of the dielectric constant and the experimental one (Ref. 3).

	Peak energy (eV)					
	$P_{I}$	$P_{II}$	$P_{III}$	$P_{IV}$		
Theoret.	5.9	7.2	8.5	15.4		
Exper.	5.6	7.2	9.4	14.4		

than that of the theoretical EDC by about a factor of 2 (Table II). Since the width of the peak I derived from the C 2s state can not be broaden by modifying the crystal potential, its broadening in the XPS EDC is presumably due to the lifetime broadening observed for the inner valence band of III-V compounds by Ley *et al.*<sup>13</sup> The same result is also observed for ZrC and HfC.<sup>8</sup> Nevertheless the present theoretical EDC from the APW calculation using the Slater exchange potential is on the whole in good agreement with the XPS EDC.

# **V. CONCLUSIONS**

The XPS valence-band spectrum of single-crystal TiC is in good agreement with the theoretical EDC from the present APW calculation, which uses a crystal potential based on neutral-atomiccharge densities and the Slater exchange potential.



FIG. 7. Comparison of the theoretical EDC using the Kohn-Sham exchange potential (solid line) with the corrected x-ray photoelectron spectrum (dashed line).

This APW calculation is also consistent with both the x-ray emission and absorption spectra, the low-temperature specific heat, and the optical reflectivity. The XPS spectrum supports the non-self-consistent APW calculation rather than the semi-self-consistent one.<sup>5</sup> The DOS at the Fermi level from the calculation is 0.22 elec trons/(eV primitive cell), which is nearly equal to the value of 0.23 from the low-temperature specific heat. The ratio of the peak II to the peak I in the integrated intensity is 2.9 to 1.0 from the XPS spectrum, which is nearly equal to the value of 3 to 1 from the theoretical DOS. These results show that the interplay between the XPS measurement and the APW calculation can be most rewarding for the investigation of the electronic structure of the transition metal carbides.

The present band calculation can allow us to derive the consequences about the bonding charac-

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ter of TiC, as follows: (i) The C 2s state makes few contributions to the bonding of carbon and titanium and to the  $sp^3$  hybridization of the C atom. (ii) The C 2p and Ti 3d states contribute predominantly to the covalent bond in TiC. (iii) The charge transfer from titanium to carbon mainly occurs between the Ti 4s and the C 2p states, which contributes to the ionic bond. (iv) The C atom does not form the  $sp^3$  hybrid orbitals. Then three C 2p orbitals determine the atomic configuration around the C atom, which is consistent with the rock-salt structure of TiC. (v) TiC is a semi-metal compound, and a fraction of the Ti 3d and 4s electrons contributes to the metallic bond.

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