PHYSICAL REVIEW B VOLUME 34, NUMBER 6 15 SEPTEMBER 1986

Defect states in substoichiometric tantalum carbide

G. R. Gruzalski and D. M. Zehner
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 6 January 1986)

X-ray photoelectron spectroscopy was used to determine core-level binding energies (BE's) and valence-band structure for TaC_x over the range $0.5 \lesssim x \lesssim 1.0$. As x decreased from about 1.0 to about 0.5, the tantalum $4d$ and $4f$ BE's shifted toward the Fermi level by about 0.8 eV and the p-d valence-band peak shifted by about 0.6 eV. The carbon $2s$ BE was difficult to determine precisely, but it too appeared to shift toward the Fermi level as x decreased, though by a smaller amount than did the p-d valence-band peak. The carbon $1s$ BE shifted by yet a smaller amount, and possibly even remained constant for $x > 0.6$. Also, the relative intensity in the valence-band spectra between about 1 and 2 eV BE increased as x decreased. These observations are explained in terms of (i) an added negative charge in the vicinity of tantalum atoms owing to the presence of carbon vacancies and (ii) the corresponding redistribution of tantalum states, i.e., the formation of occupied defect states. In addition, as x decreased it appears that charge may have transferred away from carbon atoms remaining in the crystal.

I. INTRODUCTION

Understanding the electronic structure of group-IVB and -VB transition-metal monocarbides has been a long-standing objective, and efforts to this end have been relatively successful for the stoichiometric monocarbides. Calculations have shown that the electronic structures of all these stoichiometric monocarbides are similar: Each consists of a low-lying band primarily derived from carbon $2s$ states and, separated from this band by an energy gap, several overlapping bands primarily derived from carbon $2p$ and metal d states. The density of states (DOS) of these p-d bands are made up of two parts separated by a minimum, near which lies the Fermi energy E_F; the lower- and higher-energy parts are mainly p- and d-like, respectively. In many cases this description of the electronic structure has been borne out by experiment.[1]

The search for a satisfactory understanding of the electronic structure of the substoichiometric carbides (i.e., those deficient in carbon) has been relatively recent. Theoretical work has concentrated on titanium[2-6] and niobium[7-12] carbides, though calculations also have been made for carbides of vanadium,[6] zirconium,[10] hafnium,[9] and tantalum.[9] Two of these studies[2,9] have suggested that removing carbon has little effect upon the shape of the DOS (other than a broadening of the sharp features), but the others have suggested that new "defect" states are formed, that these states are associated with carbon vacancies, and that their lowest energies lie near the minimum in the DOS of the p-d bands. For substoichiometric titanium carbide (denoted as TiC_x), the calculations show that the defect states lie just above[3] or just below[4-6] E_F; for VC_x, ZrC_x, and NbC_x they are found to lie between about 1.0 and 2.7 eV below E_F.[6-8,10-12]

Few experimental investigations have supplied information relevant to the question of whether or not these defect states exist; those that have, however, are more or less consistent with the theoretical studies suggesting that defect states do form, and that they form below E_F. Regarding the group-IVB carbides, the only work of which we are aware has been on TiC_x. Pflüger *et al.*[13] have interpreted their carbon K characteristic-loss spectra as indicating that E_F remained constant (presumably with respect to the carbon $1s$ level) as the carbon-to-titanium ratio x was varied in this material from 0.6 to 1.0. From this observation they have inferred that new states were created below E_F as carbon was removed. (Because of the charge transfer in these materials, removing carbon would result in charge being transferred back to the transition metal in such a way that would cause E_F to increase, were new states not created at or below the original Fermi level; see discussion in Sec. IV.) Defect states in this material were observed directly in x-ray emission spectra by Gubanov and coworkers[14] and in photoemission spectra by Hagström *et al.*;[15] these states were near 1 eV binding energy (BE), in qualitative agreement with theoretical predictions.[4-6] Regarding the group-VB carbides, the relevant experimental work of which we are aware has been done on NbC_x. In particular, Höchst *et al.*[16] have observed intensity near 1.9 eV BE in the valence-band spectrum of $NbC_{0.85}$, which they have attributed to defect states associated with carbon vacancies in qualitative agreement with theory.[7,8,10-12] Similar results also have been obtained in related experimental studies[17-20] on group-IVB nitrides, which are believed to be structurally and electronically similar to the group-VB carbides. Hence, the emerging picture appears to be that defect states associated with carbon vacancies do indeed form and that their lowest energies lie below E_F. Of course, additional studies of other substoichiometric carbides will be required to verify this induction.

In a previous study[21] it was shown that the valence- and conduction-band spectra of single-crystalline nearly stoichiometric TaC are consistent with the DOS obtained from augmented-plane-wave calculations.[9] During that study it was found that near-surface TaC_x regions of various compositions (and degrees of order) could be prepared. This was accomplished by first sputtering with argon ions (which left the near-surface region carbon deficient) and then annealing in a controlled manner (which not only allowed the damaged near-surface region to reorder but also allowed carbon to diffuse from the bulk to the surface region, producing the desired near-surface composition). Hence, it was recognized that the above ideas regarding defect states could be tested by using surface-science techniques to probe variously prepared near-surface regions of a single specimen of tantalum carbide. This course was pursued by using x-ray photoelectron spectroscopy (XPS) to determine core-level binding energies (BE's) and valence-band structure of several near-surface regions, which varied in composition from $x \simeq 0.5$ to $x \simeq 1.0$. Auger electron spectroscopy (AES) measurements were made also. In this paper our observations are summarized, and they are interpreted in terms of (i) an added negative charge in the vicinity of tantalum atoms owing to the creation of carbon vacancies and (ii) the corresponding redistribution of tantalum states, i.e., the formation of occupied defect states. Also, an argument is presented which suggests that as x decreases charge may be transferring away from carbon atoms remaining in the crystal.

II. EXPERIMENTAL INFORMATION

Measurements were made in an ion-pumped UHV chamber having a base pressure of less than 10^{-8} Pa and equipped with a double-pass cylindrical mirror analyzer (CMA) containing a coaxial electron gun, an unmonochromatic aluminum x-ray source [$E(\mathrm{Al}K\alpha)=1486.6$ eV], low-energy electron diffraction (LEED) optics, and a quadrupole mass spectrometer. XPS data were obtained with the CMA operated in the retarding mode (15-eV pass energy, about 1.2-eV resolution); AES data were obtained with the CMA operated in the nonretarding, first-derivative mode (1-V peak-to-peak modulation, about 0.6% resolution). The energy scale of the spectrometer was calibrated by setting the measured gold $4f_{7/2}$ BE equal to 84.1 eV with respect to E_F and by using procedures similar to those described elsewhere.[22] Binding energies were determined from peak maxima with an overall estimated precision of ±0.1 eV.

The tantalum carbide crystal used in this study was polished to within 0.1° of the (100) plane. It was supported in the UHV chamber by a thermally insulated loop of tungsten wire (0.010-in. diam); two slots were spark cut into opposite edges of the specimen disk to accommodate the wire. An infrared pyrometer was used to monitor the surface temperature of the crystal, which was heated by bombarding its back surface with 800-eV electrons. The surfaces investigated were prepared by argon-ion bombardment (1000 V, 10 μA, 10 min) followed by anneals at temperatures up to 2600 °C. Well-resolved LEED patterns were not seen until the as-sputtered surfaces were annealed to near or above 700 °C for 10 min; very sharp (1×1) LEED patterns were seen subsequent to 10-min anneals near or above 1600 °C.

Oxygen and argon were evidenced immediately after sputtering, but no other contaminants were detected. The amount of oxygen and argon present decreased with increasing annealing temperature. If the as-sputtered surface remained at room temperature, however, the amount of oxygen present increased with time; as much as 0.1 monolayer may have been present within 50 h after sputtering. Unfortunately, it was not possible experimentally to sort out the effects of all factors that changed as a result of an anneal (e.g., the carbon-to-tantalum ratio, the degree of ordering, the amount of contaminant present). Yet, by comparing XPS valence-band and core-level spectra from as-sputtered surfaces with those from as-sputtered surfaces deliberately exposed to oxygen, we were able to show that the oxygen contaminant was an adsorbate and that its presence probably did not affect the results and conclusions presented herein. We also were able to rule out some possibilities regarding disorder (e.g., the presence of large extended defects). Moreover, it is demonstrated in this paper that the observed changes are interpretable entirely in terms of carbon-to-tantalum ratio changes.

Atomic sensitivity factors taken from Ref. 23 and areas under XPS carbon $1s$ and tantalum $4f$ lines were used to determine x, the average carbon-to-tantalum ratio in the near-surface region. The relative precision of x, which only depends upon the statistical precision of the areas and on how well differences can be determined, was estimated as ±3%. The largest values of x were within a few percent of unity, and these were obtained for well-annealed well-ordered surfaces. This value of x also was inferred from impact-collision ion-scattering spectra from similarly prepared (100) surfaces of TaC.[24] Hence, although this XPS method of determining composition often is not accurate, it appears to have been so in the present study. The bulk composition of the tantalum carbide crystal was previously estimated as being within 1% of stoichiometry.[25]

III. RESULTS AND DISCUSSION

In Fig. 1(a) are shown tantalum $4f$ XPS spectra from (100) surfaces of tantalum carbide having different carbon-to-tantalum ratios x. Also shown for comparison is one spectrum from a clean, well-ordered (100) surface of pure tantalum. The spectra are normalized so that intensities of $4f_{7/2}$ peaks are equal. As x decreases, the spectra from the tantalum carbide surfaces broaden somewhat and the valley regions between peaks fill in, suggesting there was more than one distinguishable tantalum environment in those near-surface regions deficient in carbon.

The spectra also shift toward the Fermi level as x decreases. This shift is displayed better in Fig. 2(a), which is a plot of x versus tantalum $4f_{7/2}$ BE. A similar plot is shown in Fig. 2(b) for tantalum $4d_{5/2}$. The lines in these two figures are least-squares fits of the data to straight lines constrained to have identical slope. As seen, very similar BE shifts are exhibited by the two tantalum core levels, and they are approximately linear in x. An interesting feature regarding the lines in Figs. 2(a) and 2(b) is that, when extended to their $x=0$ limits, they intercept the binding-energy axes near 21.8 eV and 226.4 eV, respectively; these values are essentially identical with 21.7 and 226.4 eV, our measured $4f_{7/2}$ and $4d_{5/2}$ BE's for pure Ta(100). (These values in turn might be compared with 21.6 and 226.4 eV, which were obtained for pure tantalum by Nyholm *et al.*[26]) Hence it appears that the tantalum $4d$ and $4f$ BE's vary nearly linearly with carbon content over an extremely wide range in composition. Ramqvist *et al.*[27] previously reported the following pairs of $4f_{7/2}$ BE's and x values for TaC_x: (23.1±0.2 eV, 0.990), (23.2±0.2 eV, 0.963), (23.1±0.2 eV, 0.887), and (23.3±0.2 eV, 0.743). The change with x in these earlier-reported BE's is smaller and, overall, in a direction opposite to that indicated by the present work.

In Fig. 1(b) are shown carbon $1s$ spectra from (100) surfaces of tantalum carbide having different values of x; the spectra are plotted so that each has the same peak height. In contrast with the tantalum $4f$ spectra, these exhibit no significant broadening with decreasing x but rather a single full width at half maximum (FWHM) of 1.43±0.06 eV, which suggests that a single carbon environment was dominant for each surface studied. Perhaps this result is not too surprising; in an ideal situation (i.e., one in which

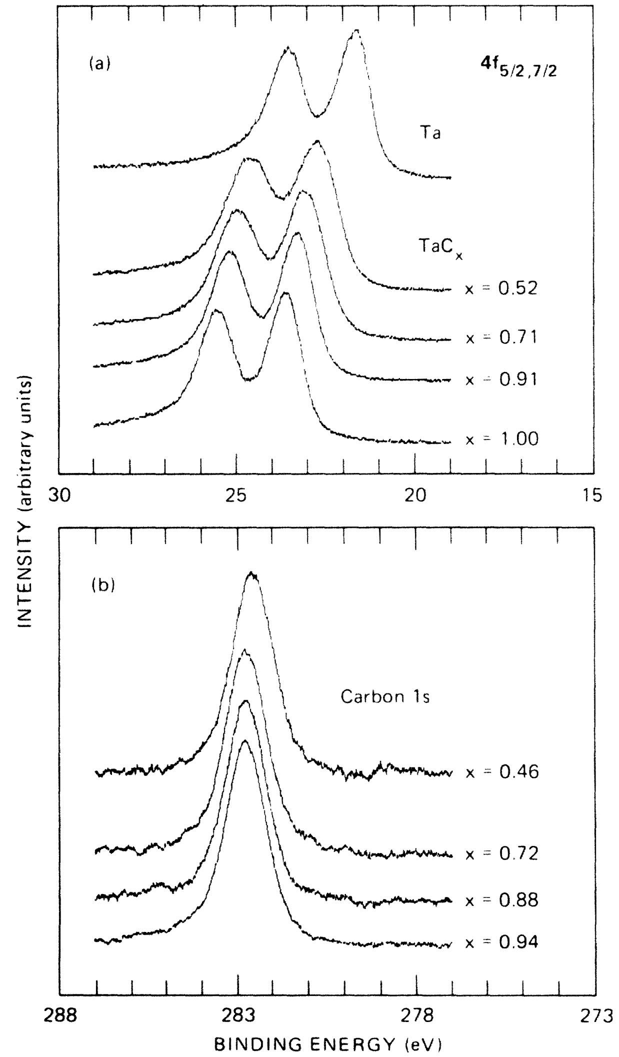

FIG. 1. (a) XPS Ta $4f$ spectra and (b) C $1s$ spectra from (100) surfaces of tantalum carbide having different carbon-to-tantalum ratios x. Also shown in (a) is one spectrum from clean, well-ordered Ta(100). Binding energies are with respect to the Fermi level.

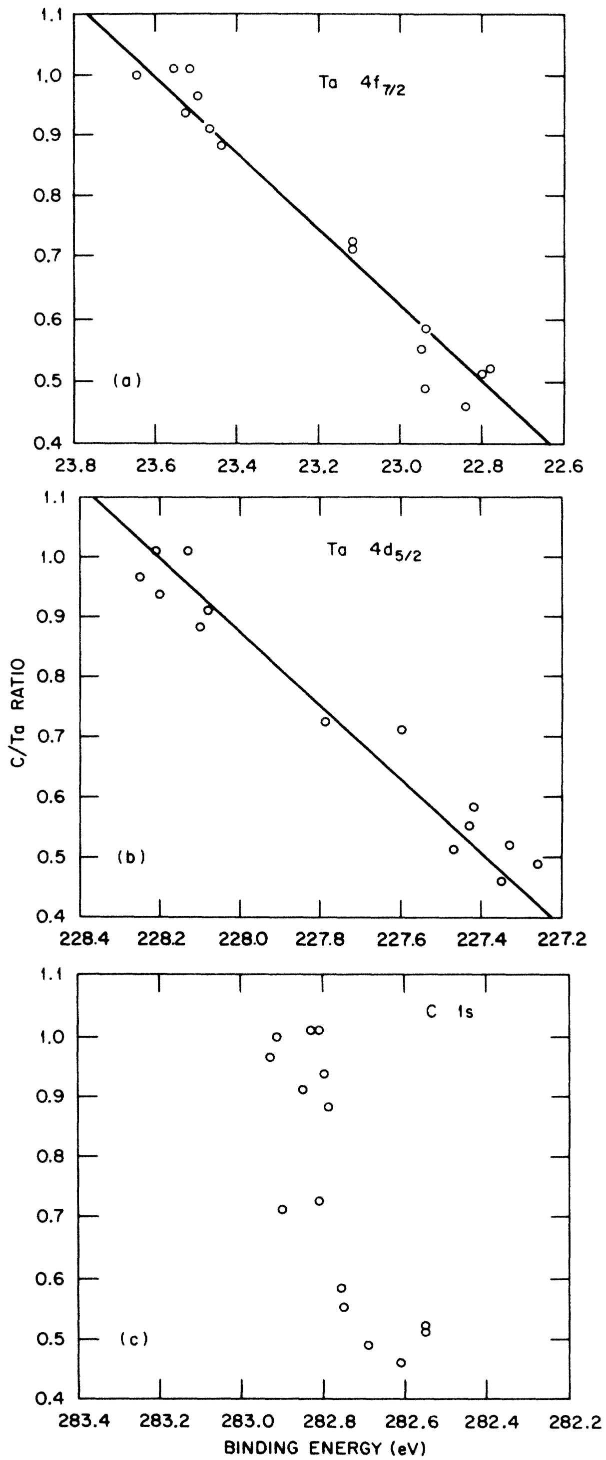

FIG. 2. Carbon-to-tantalum ratio x versus binding energy for (a) Ta $4f_{7/2}$, (b) Ta $4d_{5/2}$, and (c) C $1s$. The slope of the solid line in (a) is identical with that in (b): 0.61 per eV. The $4f_{5/2}$ and $4d_{3/2}$ BE's (not shown) are about 1.9 eV and 11.5 eV greater than the $4f_{7/2}$ and $4d_{5/2}$ BE's, respectively.

the carbon and metal atoms stay on their respective sites and no metal vacancies form), each carbon atom remains surrounded by exactly six tantalum atoms as x is varied.

Also in contrast with the tantalum spectra, the overall change in carbon 1s BE is more than a factor of 2 smaller than that for the 4d and 4f BE's [compare Figs. 2(a) and 2(b) with Fig. 2(c)]. For $x > 0.6$, the carbon 1s BE even appears to be constant (282.86±0.05 eV); if so, these data would be consistent with data obtained by others who have found that the metalloid core-level BE was independent of x for TaC_x (Ref. 27) and for ZrN_x and TiN_x (Ref. 17). Because of the scatter in the present data, however, we cannot rule out some monotonic relationship between the carbon 1s BE and x over the entire composition range investigated. Since the shift in BE is small, it is possible that a similar shift may have been present but not resolvable in the earlier studies,[17,27] for which the composition varied over a relatively narrow range. On the other hand, the data presented in Fig. 2(c) appear to suggest that most of the shift occurred for $x < 0.6$. If so, this shift may have been caused by effects other than changes in x. In particular, since the near-surface regions with smaller values of x were more disordered than those with larger values, the decrease in carbon 1s BE may have been due to defects other than carbon vacancies. Some possibilities can be ruled out. For example, we can eliminate the possibility that large extended defects were present (i.e., regions of carbon or tantalum), because the appropriate core-level BE's differed significantly from those of pure carbon (graphite) or tantalum, even for the as-sputtered surfaces. And as stated above, it appears that only one carbon environment was dominant for each surface studied, which also rules out the possibility that significant segregation took place. Nonetheless, and even though carbon vacancies may have been the dominant defect for the as-sputtered material (after all, the material is partially ionic and its vacancies tend to repel one another), we cannot experimentally rule out the possibility that other defects were playing an important role when $x < 0.6$. In any case, carbon vacancies appear to have little if any effect upon the carbon 1s BE. It is noted that the present values of the carbon 1s BE differ from those determined previously by Ramqvist *et al.*,[27] who have reported 282.1±0.2 eV BE for $x = 0.990$, 0.963, and 0.887, and 281.9±0.2 eV BE for $x = 0.743$.

In Fig. 3 the valence-band XPS spectrum from a nearly stoichiometric (100) surface of tantalum carbide is compared with $N(E)$, the total (calculated[21]) valence-band DOS broadened with an instrument resolution function (a Gaussian with 1.2 eV FWHM). The XPS spectrum is similar to that obtained by Ihara *et al.* for hot-pressed tantalum carbide.[28] Three peaks are prominent in the spectrum: The one near 12 eV BE is due in part to carbon 2s states; the one near 5 eV BE to carbon 2p and tantalum 5d states; and the one near 0.6 eV BE to a nonzero DOS at the Fermi level, primarily made up of tantalum d states of T_{2g} symmetry. Two comments should be made regarding the agreement between these curves. First, the relatively large intensities of the experimental spectrum at energies corresponding to the bottom of the valence band are due to inelastically scattered electrons and, moreover, to α_3 and α_4 x-ray satellite excitations of tantalum 4f electrons; $\alpha_3(4f_{7/2})$ and $\alpha_4(4f_{5/2})$ excitations appear near 13.7 eV BE and the $\alpha_4(4f_{7/2})$ excitation appears near 11.8 eV BE, which unfortunately overlaps structure owing to photoemission from carbon 2s states. Second, matrix-element effects have not been included in the theoretical spectrum; this simplification should not significantly affect peak locations, but it may be responsible for the intensities of the peaks near 7.0 and 0.6 eV BE being relatively large and small, respectively, in comparison with those in the experimental spectrum.

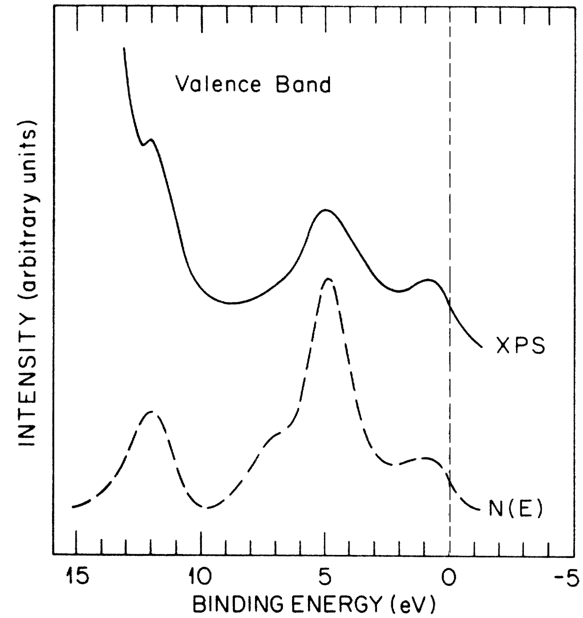

FIG. 3. Comparison of XPS valence-band spectrum (solid curve, drawn smoothly through data not shown) from nearly stoichiometric TaC(100) with theoretical spectrum (dashed curve, generated as described in Ref. 21).

Shown in Fig. 4 are valence-band XPS spectra from

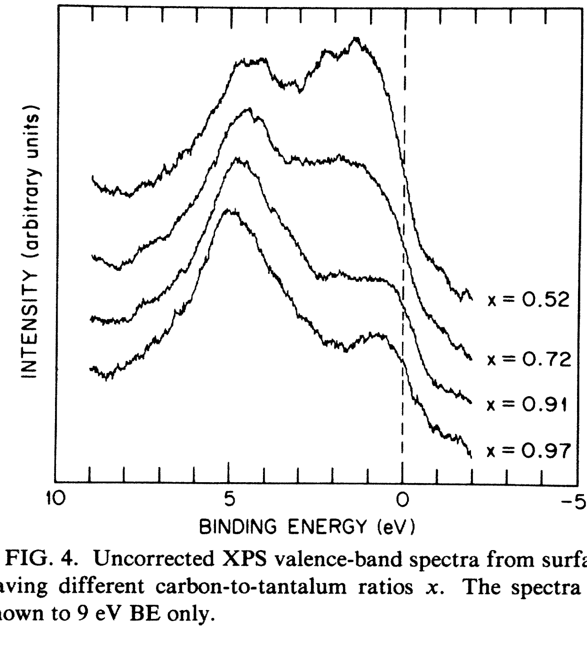

FIG. 4. Uncorrected XPS valence-band spectra from surfaces having different carbon-to-tantalum ratios x. The spectra are shown to 9 eV BE only.

surfaces of different x. The spectra are normalized so that maximum intensities are equal. As x decreases from 0.97 to 0.52, the peak near 5 eV BE shifts toward E_F by about 0.6 eV. The lower-lying carbon $2s$ peak (not shown) also appears to shift somewhat and in the same direction, but the extent of this shift is very difficult to determine because it is smaller (though not as small as that of the carbon $1s$ level) and because the carbon $2s$ peak overlaps structure owing to x-ray satellite excitations of tantalum $4f$ electrons, as discussed above. In addition, it can be seen that the relative intensity in the spectra between about 1 and 2 eV BE increases as x decreases. As already mentioned, similar valence-band structure has been observed previously for related systems[14–20] and has been attributed to photoemission from defect states associated with metalloid vacancies. In some[16–20] of these earlier studies, however, the valence-band peak owing to metalloid-metal hybridization was not observed to shift as x was varied.

Shown in Fig. 5(a) are carbon *KVV* AES spectra from surfaces of different x. The spectra, which were obtained with a primary-beam energy of 3 keV, are normalized so that the maximum peak-to-peak intensities are equal. Qualitatively the spectra are similar to each other and to the carbon *KVV* spectrum for tantalum carbide previously reported by Shul'ga and Gutsev.[29] Nonetheless, differences in the spectra can be seen. For example, the shape of the spectra clearly changes with x near 260 and 275 eV, and the intensity ratio I_{pp}/I_{ss} decreases as x decreases, where I_{pp} and I_{ss} are peak-to-peak amplitudes of the AES signals near 270 and 250 eV, respectively. (These designations denote that the corresponding features arise from Auger transitions involving carbon $2p$ and $2s$ electrons, respectively.) For comparison, an AES spectrum showing both carbon and tantalum lines is given in Fig. 5(b); this spectrum was obtained with a primary-beam energy of 2 keV. Most of the intensity of the tantalum signal in this spectrum arises from transitions involving $4d$ holes and $4f$ electrons.

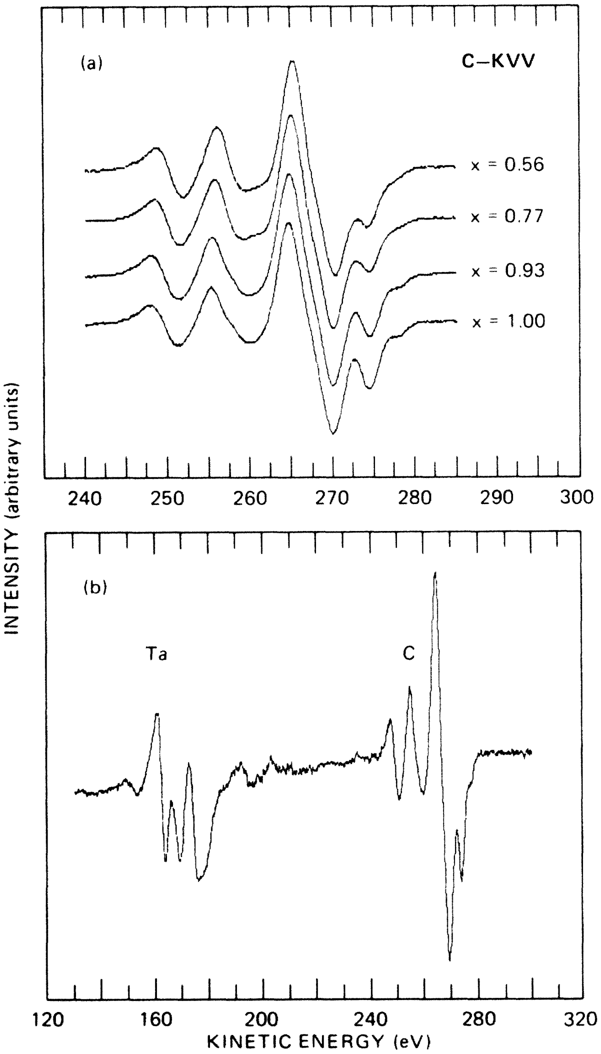

FIG. 5. (a) Carbon *KVV* AES spectra from surfaces having different carbon-to-tantalum ratios x. (b) AES spectrum showing both carbon and tantalum lines from nearly stoichiometric TaC(100).

Two results presented above (the direction of the shift of the tantalum $4f$ BE as x varied and the value of the carbon $1s$ BE) differ from those reported earlier.[27] Although these differences are not fully understood, we suggest that the hydrocarbon contamination present in the earlier work probably was *not* a factor; we state this because our data for as-inserted tantalum carbide show that surface contamination from mechanical polishing and exposure to air had little effect upon the core-level BE's reported herein. It is more likely that the difference in the direction of the core-level shift is due to a tacit assumption made by the earlier investigators: that the measured bulk compositions of the hot-pressed materials did not differ from the (unmeasured) compositions of the near-surface regions sampled by their XPS measurements. The difference in carbon $1s$ BE's is more difficult to explain, but almost certainly is due to differences in the calibration and linearity of the spectrometers.

IV. INTERPRETATION

The core-level and valence-band XPS results are summarized schematically in Fig. 6(a). Note that the energy scales in this figure, like those in Figs. 1—4, are not absolute energy scales but rather are relative to the appropriate Fermi level $E_F(x)$. In this section the experimental results summarized in Fig. 6(a) are interpreted in terms of the redistribution of charge caused by the presence of carbon vacancies.

When tantalum and carbon combine to form tantalum carbide, charge is transferred from tantalum atoms to carbon atoms.[9] This charge transfer makes a substantial contribution to the sizable core-level shifts that accompany the formation of the carbide. Hence, in light of the tantalum core-level shifts shown in Figs. 2(a) and 2(b), it may be reasonable to assume that, when a carbon atom is removed, the "tantalum" electrons that would have transferred to that carbon atom remain instead in the vicinity of the tantalum atoms. In addition to this interpretation being intuitive, it is consistent with theoretical results for TiC_x in Ref. 4, in that those results show a net transfer of charge to titanium states as x decreases.

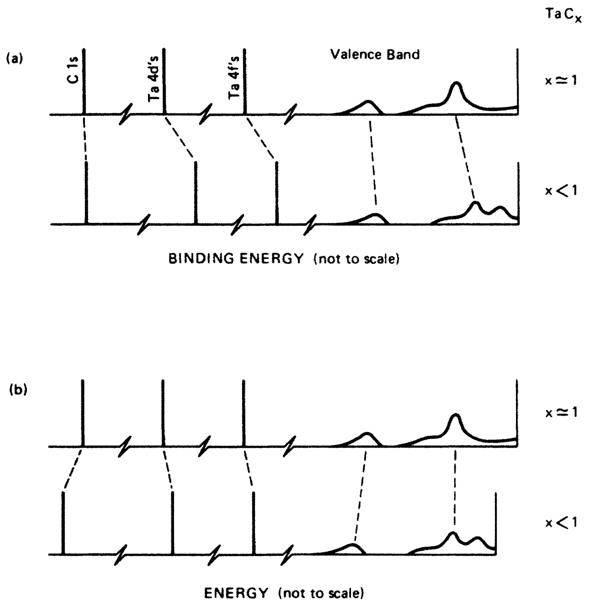

FIG. 6. Schematic of XPS results showing changes in the electronic structure of TaC_x as x is varied. Energy scales are (a) relative to the appropriate Fermi level $E_F(x)$ and (b) to the crystal zero.

The shift of the p-d valence-band peak toward E_F with decreasing x also is consistent with the idea that a decrease in x results in added negative charge in the vicinity of the tantalum atoms. That this shift is smaller than the corresponding shift of the tantalum $4d$ and $4f$ core levels may be ascribed to hybridization effects. It should be noted, however, that similar shifts of "metalloid-metal" valence-band peaks are not observed in all substoichiometric transition-metal carbides and nitrides. For example, in studies of NbC_x,[16] TiN_x,[17-19] and ZrN_x,[17,19,20] the valence-band peak in question was not observed to shift with x. Such observations are contrary to what one might expect from a generalization of the present data or of the data for TiC_x,[14,15] and they are contrary to what is predicted theoretically.[6,10,30] In addition, the core-level shifts previously determined for these systems are either inconsistent (compare Ref. 17 with Ref. 18) or suspect (see last paragraph of Sec. III regarding Ref. 27). It appears, therefore, that further work will be required before one can determine whether the ideas presented in this paper regarding charge redistribution hold for other substoichiometric transition-metal carbides and nitrides.

The additional intensity appearing in the valence-band spectra between about 1 and 2 eV BE is interpreted as being due to photoemission from occupied defect states that were created as carbon was removed. Since the local carbon environment did not appear to gain negative charge as x decreased (see below), it can be inferred that the defect states likely are localized in the vicinity of the carbon vacancies. The changes observed in the tantalum core-level BE's, however, probably rule out the possibility that these states are extremely well localized in the vacancy sites themselves. It is therefore suggested that the defect states primarily are localized on those tantalum atoms which neighbor carbon vacancies and, consequently, that they primarily are tantalum states which have redistributed spatially and energetically in order to accommodate the added negative charge caused by the presence of these vacancies.

Although it was difficult for us to determine the carbon $2s$ BE, it appears that this level changed with x more than the carbon $1s$ level did. This result is surprising because it may suggest that carbon $2s$ states are mixing with tantalum states more than indicated by theory.[9] Another explanation would involve changes in the shape of the $2s$ band; results of coherent-potential-approximation calculations for TaC_x,[9] however, do not support this possibility.

Much has been written about the shift of the Fermi level $E_F(x)$ as x is varied in transition-metal carbides. One idea behind such discussion already has been introduced above: Because of the charge transfer in these materials (from metal to carbon), more than four valence-band states are emptied when a carbon atom (and, hence, four valence electrons) is removed. In a rigid-band sense, the "excess" charge that remains, which we suggest remains in the vicinity of those tantalum atoms neighboring the carbon vacancy, must occupy states just above the original Fermi level, unless new states are created below it. By determining the change in $E_F(x)$ with x, therefore, one may be able to infer whether new states were created below the original Fermi level. Of course, $E_F(x)$ must be determined with respect to some meaningful reference level, say with respect to the bottom of a rigid band or to the crystal zero (which would be identical with the vacuum zero if there were no surface-barrier potential). Since the TaC_x valence band is not rigid and since the BE's reported in this paper were measured with respect to $E_F(x)$, the present data cannot be used in a precise manner to address the question of Fermi-level motion. Similarly, we question the conclusion in Ref. 13 that $E_F(x)$ remained constant as x was varied in TiC_x.

Nonetheless, if one assumes that the changes in the valence band evidenced in Fig. 4 are similar to those recently calculated[6,10,30] for other transition-metal carbides and nitrides, one is led to a description of our data such as that shown in Fig. 6(b). In particular, this figure was constructed by assuming that as x varies the position of the p-d valence-band peak changes very little with respect to the crystal zero (the calculated[6,10,30] energies were with respect to "muffin-tin" zeros). If this figure is an accurate description of what happens in tantalum carbide as carbon vacancies are created, then in addition to what already has been said about the redistribution of charge accompanying the formation of carbon vacancies, one might further suppose (again in an intuitive way, though this time based upon the shift of the carbon $1s$ potential) that, as x decreases, charge transfers away from the carbon atoms remaining in the crystal. This interpretation is consistent with our present understanding of the AES spectra[31] shown in Fig. 5(a) and with the theoretical results given in Ref. 4, in that those results show a decrease in the amount of charge associated with carbon atoms as x decreases in TiC_x. It is as if the carbon $2p$ and tantalum defect states were competing for electrons.

It should be noted that factors in addition to those explicitly considered above may contribute to energy-level shifts.[32] For example, it can be inferred from the change in lattice parameter[33] with x that the ratio of the molar volume of TaC_x to the molar volume of the appropriately weighted sum of tantalum and carbon is less than unity and, moreover, that it decreases as x increases; the corresponding compression of electron charge likely causes all affected levels to shift to higher energies as x increases. There also are effects on levels associated with a given atom that arise from charge flow in the medium surrounding that atom; for example, if the ideas presented above regarding charge redistribution are correct, as x decreases there would be a contribution of the Madelung form that likely would shift occupied carbon and tantalum levels to higher and lower energies, respectively. In addition, there may be relaxation, correlation, and configuration changes with x that are not even associated with charge flow but that can bring about changes in BE's. Moreover, all of these factors can be of the same order. Our interpretation should therefore be thought of as tentative, even though the factors we have explicitly considered may be the most significant ones.

V. CONCLUDING REMARKS

XPS was used to determine core-level binding energies and valence-band structure for TaC_x over the composition range $0.5 \lesssim x \lesssim 1.0$. The near-surface regions studied were prepared by argon-ion bombardment (which left them carbon deficient) and subsequent anneals. The anneals not only allowed the near-surface regions to order but also allowed x to increase, because of carbon diffusion from the bulk. The degree of ordering varied as x varied, however, and this may have affected our results. Nonetheless, it was demonstrated that these results, which are summarized below, could be understood in terms of (i) an added negative charge in the vicinity of tantalum atoms owing to the presence of carbon vacancies and (ii) the corresponding redistribution of tantalum states, i.e., the formation of occupied defect states. An argument also was presented which suggests that as x decreases charge may be transferring away from carbon atoms remaining in the crystal.

As x decreased from about 1.0 to about 0.5 (i) the carbon $1s$ BE changed very little if at all for $x > 0.6$, (ii) the carbon $2s$ BE shifted toward the Fermi level, although the extent of the shift was small and difficult to determine, (iii) the position of the p-d valence-band peak shifted toward the Fermi level by about 0.6 eV, and (iv) the tantalum $4d$ and $4f$ BE's shifted toward the Fermi level by about 0.8 eV. It is emphasized that the magnitude of these shifts increased in the order the shifts are listed. Also, the relative intensity in the valence-band spectra between about 1 and 2 eV BE increased as x decreased.

ACKNOWLEDGMENTS

We thank P. Marksteiner, A. Neckel, G. M. Stocks, and R. E. Watson for their careful reading and useful comments regarding an earlier version of this paper, and we are grateful to G. W. Ownby for technical assistance. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

---

[1] For a review of both theoretical and experimental work, see A. Neckel, Int. J. Quantum Chem. **23**, 1317 (1983).

[2] J. Klima, J. Phys. C **12**, 3691 (1979).

[3] L. M. Huisman, A. E. Carlsson, C. D. Gelatt, Jr., and H. Ehrenreich, Phys. Rev. B **22**, 991 (1980).

[4] V. A. Gubanov, A. L. Ivanovsky, G. P. Shveikin, and D. E. Ellis, J. Phys. Chem. Solids **45**, 719 (1984).

[5] J. Redinger, R. Eibler, P. Herzig, A. Neckel, R. Podloucky, and E. Wimmer, J. Phys. Chem. Solids **46**, 383 (1985).

[6] P. Marksteiner, P. Weinberger, A. Neckel, R. Zeller, and P. H. Dederichs, Phys. Rev. B **33**, 812 (1986).

[7] K. Schwarz and R. Rösch, J. Phys. C **9**, L433 (1976).

[8] G. Ries and H. Winter, J. Phys. F **10**, 1 (1980).

[9] B. M. Klein, D. A. Papaconstantopoulos, and L. L. Boyer, Phys. Rev. B **22**, 1946 (1980).

[10] P. Marksteiner, P. Weinberger, A. Neckel, R. Zeller, and P. H. Dederichs, Phys. Rev. B **33**, 6709 (1986).

[11] P. Pecheur, G. Toussaint, and E. Kauffer, Phys. Rev. B **29**, 6606 (1984).

[12] W. E. Pickett, B. M. Klein, and R. Zeller, Phys. Rev. B **34**, 2517 (1986).

[13] J. Pflüger, J. Fink, G. Crecelius, K. P. Bohnen, and H. Winter, Solid State Commun. **44**, 489 (1982).

[14] V. A. Gubanov, E. Z. Kurmaev, and D. E. Ellis, J. Phys. C **14**, 5567 (1981); A. L. Ivanovsky, V. A. Gubanov, G. P. Shveikin, and E. Z. Kurmaev, J. Less-Common Met. **78**, 1 (1981).

[15] A. L. Hagström, L. I. Johansson, S. B. M. Hagström, and A. N. Christensen, J. Electron Spectrosc. Relat. Phenom. **11**, 75 (1977); see also, L. I. Johansson, A. L. Hagström, B. E. Jacobson, and S. B. M. Hagström, *ibid.* **10**, 259 (1977).

[16] H. Höchst, P. Steiner, S. Hüfner, and C. Politis, Z. Phys. B **37**, 27 (1980).

[17] H. Höchst, R. D. Bringans, and P. Steiner, Phys. Rev. B **25**, 7183 (1982).

[18] L. Porte, L. Roux, and J. Hanus, Phys. Rev. B **28**, 3214 (1983).

[19] R. D. Bringans and H. Höchst, Phys. Rev. B **30**, 5416 (1984).

[20] L. Porte, Solid State Commun. **50**, 303 (1984).

[21] G. R. Gruzalski, D. M. Zehner, and G. W. Ownby, Surf. Sci. **157**, L395 (1985).

[22] C. J. Powell, N. E. Erikson, and T. Jach, J. Vac. Sci. Technol. **20**, 625 (1982).

[23] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, in *Handbook of X-Ray Photoelectron Spectroscopy*, edited by G. E. Muilenberg (Perkin-Elmer Corporation, Eden Prairie, MN, 1979), p. 188.

[24] C. Oshima, R. Soudia, M. Aono, S. Otani, and Y. Ishizawa, Phys. Rev. B **30**, 5361 (1984).

[25] H. G. Smith and W. Glaser, Phys. Rev. Lett. **25**, 1611 (1970).

[26] R. Nyholm, A. Berndtsson, and N. Mårtensson, J. Phys. C **13**, L1091 (1980). The energy scale of the spectrometer in this previous work was calibrated by setting the measured gold $4f_{7/2}$ BE equal to 84.0 eV. We use 84.1 eV.

[27] L. Ramqvist, K. Hamrin, G. Johansson, U. Gelius, and C. Nordling, J. Phys. Chem. Solids **31**, 2669 (1970).

[28] H. Ihara, M. Hirabayashi, and H. Nakagawa, Phys. Rev. B **14**, 1707 (1976).

[29] Ju. M. Shul'ga and G. L. Gutsev, J. Electron Spectrosc. Relat. Phenom. **34**, 39 (1984).

[30] J. Klima, G. Schadler, P. Weinberger, and A. Neckel, J. Phys. F **15**, 1307 (1985).

[31] Differences in the carbon *KVV* AES spectra from surfaces of different x will be addressed in a later work.

[32] For example, see R. E. Watson and M. L. Perlman, Phys. Scr. **21**, 527 (1980).

[33] E. K. Storms, *The Refractory Carbides* (Academic, New York, 1967), p. 89.