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Photoemission resonance effects in the nitrides of titanium and zirconium

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Photoemission measurements have been carried out on TiN, $TiN_{0.80}$, ZrN, and $ZrN_{0.82}$ in the photon energy range 15—150 eV. A resonant enhancement of the *d* states was seen at $h\nu=42$ and 32 eV, respectively, for the Ti and Zr nitrides. The energy for this enhancement is significantly greater than the binding energy of the Ti 3*p* and Zr 4*p* core levels as measured in photoemission. No resonant enhancement was seen for the vacancy state in nonstoichiometric $TiN_{0.80}$ indicating that the state has mainly non-*d*-type character.

I. INTRODUCTION

Titanium nitride, TiN, and zirconium nitride, ZrN, are metallic and exhibit the high electrical conductivity, high melting point and hardness characteristic of the refractory transition-metal carbides and nitrides. The electronic properties of these materials are thus of considerable interest. In an earlier study[1] the electronic structure of the titanium and zirconium nitrides was studied with ultraviolet and x-ray photoelectron spectroscopy. In agreement with several theoretical studies, it was found that the valence-band region consists of metal *d* states which are strongly hybridized with the nitrogen 2*p* states, and that the nitrogen 2*s* states are about 17 eV below the Fermi energy. A detailed comparison was made with the density of states calculated by Neckel *et al.*[2] for TiN and good qualitative agreement was found. Some more quantitative aspects were not so well described. The calculation, for example, predicted a high density of states at the Fermi energy, with almost pure Ti 3*d* character. Our photoemission experiments made with a range of photon energies (16.9, 21.2, 40.8, and 1487 eV) failed to show the intensity variation expected for a pure Ti 3*d* density of states at the Fermi energy.

Substoichiometric samples of TiN and ZrN were also examined, and the photoemission spectra were compared with the density of valence-band states calculated by Klima[3] using the coherent-potential-approximation method. Again, the trends in the data on going from the stoichiometric to the substoichiometric materials were shown to be well explained by the calculation. The experiment, however, revealed a new peak at a binding energy of 2 eV for the substoichiometric materials which was not predicted by the theory. It was concluded that this new peak represented an occupied defect state. Recent x-ray photoemission spectroscopy (XPS) results from Porte *et al.*[4] on thin films produced by reactive sputtering also exhibit this defect state and show that it systematically decreases in intensity as the material becomes more stoichiometric. It is not clear why this defect state has not been seen by Johansson *et al.*[5] and Johansson and Callenas[6] in angle-resolved photoemission studies on the (001) face of single crystal $TiN_{0.83}$. One possibility is that the flash-heating method used to clean their samples changes the stoichiometry near the surface. These authors do, however, see a surface state at 2.9 eV below the Fermi energy. The surface state, which shows little or no dispersion, has been associated with the Δ_5 band and thus arises from the p_x and p_y orbitals on the nitrogen atoms.[7] We have not seen such a surface state in our angle-integrated measurements on polycrystal surfaces of TiN and $TiN_{0.80}$.

The present work utilized the tunability of synchrotron radiation to study in greater detail the electronic structure of the titanium nitrides, and zirconium nitrides, both stoichiometric and substoichiometric. The photon-energy dependence of photoionization cross sections enables one to determine the atomic character of specific regions of the density of states by observing how relative photoemission intensities change. In particular we examined the behavior of the photoemission from the region near the Fermi energy as a function of the photon energy. In addition to variations caused by the photoionization cross sections, we also found strong resonances in the metal *d* emission. These effects, which are described in detail in Sec. III, are related to the metal *p*-*d* excitation and provide further information about the atomic character of the occupied states.

II. EXPERIMENTAL DETAILS

Crystals of almost stoichiometric TiN and ZrN were grown using a chemical-vapor-deposition technique. The substoichiometric crystals were prepared with a traveling solvent method in which a bar of the pure metal was heated under a high pressure (~20 atm) of nitrogen. Both growth techniques are described in more detail in Ref. 1 along with the results of characterization of the samples. The samples used in this study had compositions of $TiN_{0.99}$, $TiN_{0.80}$, $ZrN_{0.97}$, and $ZrN_{0.82}$. For brevity we will refer to the almost stoichiometric materials as TiN and ZrN.

The photoelectron spectra were measured with synchrotron radiation from the storage ring DORIS in Hamburg. The Flipper I monochromator was used to provide monochromatic radiation in the photon energy range 15—150 eV and the spectra were measured with a cylindrical mirror analyzer. The combined energy resolution of the monochromator and analyzer varied from 0.25 eV at $h\nu=20$ eV to 0.50 eV at $h\nu=150$ eV.

The samples studied were polycrystalline and were cleaned *in situ* with a diamond file prior to measurement. This method allows a clean surface to be produced without causing unwanted changes in the composition. The alternative techniques of argon-ion sputtering or high-temperature flashing on the other hand, may cause compositional changes at the surface.

III. RESULTS AND DISCUSSION

Photoemission electron distribution curves for the valence-band region of TiN, $\mathrm{TiN_{0.80}}$, ZrN, and $\mathrm{ZrN_{0.82}}$ were measured with photon energies $h\nu$ varying between 15 and 150 eV. A strong increase in the emission near the Fermi energy was found as $h\nu$ increased beyond 42 eV for TiN and $\mathrm{TiN_{0.80}}$ and beyond 32 eV for ZrN and $\mathrm{ZrN_{0.82}}$. Spectra for the energy region near this enhancement are shown in Fig. 1 for TiN. The partial densities of states for TiN calculated by Neckel *et al.*[2] are also shown for comparison. The partial densities of states can be seen to reproduce qualitatively the width of the valence band and the shape for the $h\nu=40$ eV spectrum of TiN. The large change between the $h\nu=40$ eV and $h\nu=45$ eV spectra, however, cannot be explained by variation of photoionization cross section alone and must be due to a multielectron effect.

To obtain a more comprehensive picture of the resonance, constant-initial-state (CIS) measurements were carried out. The photon energy and the electron kinetic energy were scanned simultaneously so that the electron binding energy remained constant. CIS curves are shown in Fig. 2 for binding energies corresponding to the peak near the Fermi energy ($E_i=0.4$ eV), the maximum of the valence band ($E_i=4.9$ eV) and the shoulder at 6.7 eV. It can be seen that the Ti $3d$ derived peak near the Fermi energy has a strong resonance with a Fano-type line shape.[8] The valence band is a mixture of Ti $3d$ and N $2p$, and calculations predict that the d-like character decreases with increasing binding energy. This can be seen in the density of states of Neckel *et al.*[2] in Fig. 1 and in the band structure by Schwartz.[9] The data seem to support this distribution: At 6.7 eV there is very little resonance while the behavior at 4.9 eV shows a distinct resonance associated with the greater Ti $3d$ density of states in this region of the valence band.

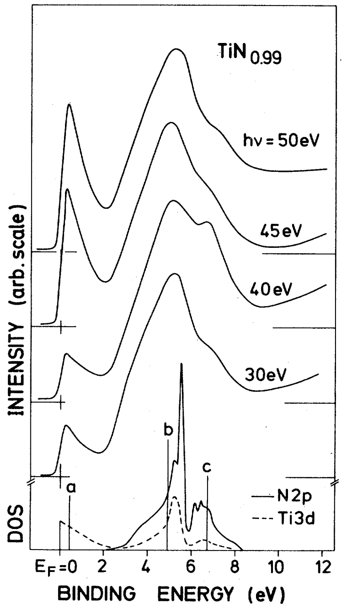

FIG. 1. Valence-band photoemission spectra for TiN obtained with photon energies of 30, 40, 45, and 50 eV. The spectra have been normalized to the highest point of the valence band. Partial densities of states from Ref. 2 are shown for comparison.

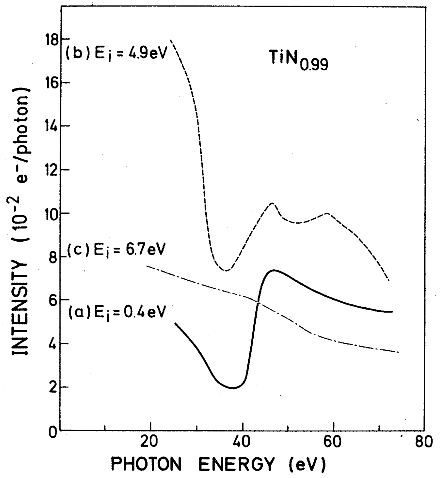

FIG. 2. Constant-initial-state curves corresponding to the labels (a), (b), and (c) in Fig. 1.

Qualitatively, these effects can be explained by resonances due to transitions of the super Coster-Kronig type, in which the additional photoemission intensity arises as the photon energy becomes greater than the Ti $3p$ binding energy. The transition

$$\mathrm{Ti}\ 3p^6\ 3d^2 \rightarrow \mathrm{Ti}\ 3p^5\ 3d^3$$

is followed by the Auger process

$$\mathrm{Ti}\ 3p^5\ 3d^3 \rightarrow \mathrm{Ti}\ 3p^6\ 3d^1 + e$$

yielding the same final state as direct photoemission from a Ti $3d$ state. The resonance observed for TiN near 43 eV is at a much higher energy than the binding energy for the Ti $3p$ level. This difference is shown in Fig. 3 which superimposes the CIS spectrum for $E_i=0.4$ eV and the photoemission spectrum taken with $h\nu=150$ eV. It can be seen that the resonance is delayed by ~ 10 eV. This discrepancy does not occur for Ni compounds, for example, where the Ni $3p$ binding energy, the antiresonance of the Ni $3d$ states in the valence band, and the resonance of the 6 eV satellite coincide to within 1 eV.[10]

The resonance in TiN does, however, take place at the same energy as the absorption threshold for the $3p \rightarrow 3d$ optical transition in $\mathrm{TiF_3}$. Absorption spectra for halides of all the $3d$ transition metals have been measured by Shin *et al.*[11] They found that the energy at the $3p \rightarrow 3d$

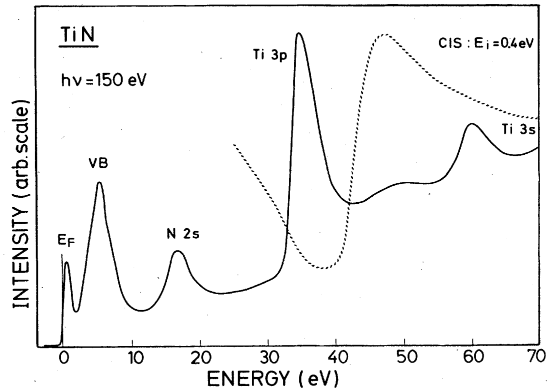

FIG. 3. Comparison for TiN of the conduction-band resonance, plotted as a function of photon energy, and the photoemission spectrum for $h\nu=150$ eV plotted as a function of binding energy. The figure shows a delay between the Ti $3p$ threshold and the resonance energy.

threshold for TiF_3 is 43 eV, in agreement with the result that we get for the resonance in TiN. Comparison of the data of Shin *et al.* with the binding energies of the $3p$ core levels for the $3d$ elements[12] reveals a close agreement for the metal atoms with more than half-filled d orbitals and an increasing deviation as one goes to atoms with fewer d electrons. This result is consistent with the good agreement between the $3p$ threshold and the resonance in the Ni compounds[10] and the delayed resonance for TiN.

A delayed resonance in Ti and TiO_2 has been reported recently by Bertel *et al.*[13] These authors show a CIS curve for Ti which is similar in shape to curve (a) in Fig. 2 of the present paper (resonance of the states near the Fermi energy for TiN) and has the same energy position to within 1 eV. They also see a much weaker resonance of the valence band in heavily oxidized Ti. Bertel *et al.* attribute the delay in the onset of the Ti resonance to the exchange interaction in the p^5d^{n+1} configuration. It was argued that the interaction should be much stronger for the transition metals with less than five electrons in the $3d$ shell than it is for those with five or more electrons.[13] Calculated $(3p,3d)$ exchange integrals for the first-row transition elements,[14] however, show a gradual increase on going through the series Sc to Ni (except for a 2% decrease between V and Cr).

A. Nonstoichiometric TiN

Resonance effects provide a very powerful tool for examining changes in the local density of states which are due to the charge transfer associated with alloying or compound formation. In this section we will compare results for TiN with those for $TiN_{0.80}$ which also show a resonance of the states just below the Fermi energy. In order to make a reliable comparison between TiN and $TiN_{0.80}$ we have taken the ratio of the area under the conduction-band peak (i.e., between the Fermi energy and 2.1 eV) to the area under the valence-band peak (2.1 to 8.5 eV). The photon-energy dependence of this ratio is seen in Fig. 4 for both materials and is compared with the ratio expected for TiN from changes in the photoionization cross section.[15] It can be seen that the onset takes place for $TiN_{0.80}$ at the same energy as for TiN but that it is much stronger, indicating that the charge transfer increases the d-like density of states. In addition to the onset at resonance, features at photon energies of 73 and 130 eV are seen in the ratio curves. The peaks at 73 and 130 eV are not resonances because there are no excitations possible from Ti or N core levels at these energies. The effect at 73 eV can be seen from Fig. 2 to be due to the valence-band cross section decreasing faster than that at the Fermi energy. The 130-eV peak, which is also seen in the data of Johansson *et al.*,[6] must be due to small cross-section modulations which become more pronounced when the ratio is taken.

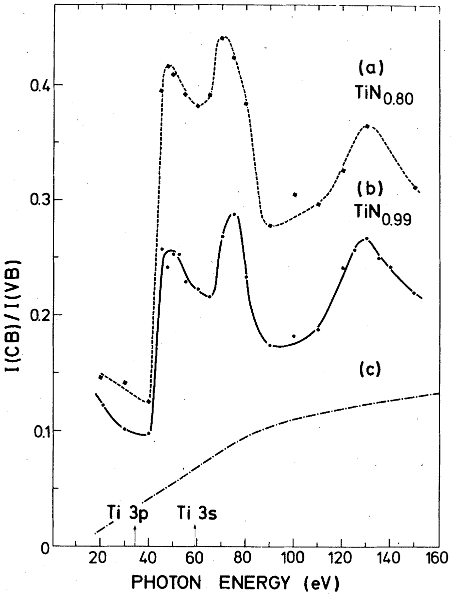

FIG. 4. Ratio of the conduction-band intensity to that of the valence band as a function of photon energy for TiN and $TiN_{0.80}$. The ratio expected from photoionization cross-section variation is shown by curve (c).

Although the resonant enhancements are similar for TiN and $TiN_{0.80}$, the difference between the intensity ratios is smaller than expected. On going from TiN to $TiN_{0.80}$, the intensity ratio increases by a factor of 1.7. This is only 75% of the value expected if we use the coherent-potential approximation calculation by Klima[3] to determine the changes in the d-like partial density of states in both the valence band and near the Fermi energy. A possible conclusion is that about 25% of the vacancy electrons are in non-d-like states and are bound at ~ 2 eV. This vacancy state, which was identified earlier,[1,17] does not show any appreciable resonance behavior. The spectra shown in Fig. 5 were taken above and below the resonance and the vacancy state (labeled as VS) does not change at all by comparison with the dramatic variation seen for the states at the Fermi energy. Lack of any resonant behavior is strong evidence for our conclusion that a significant fraction of the defect states are non-d-like.

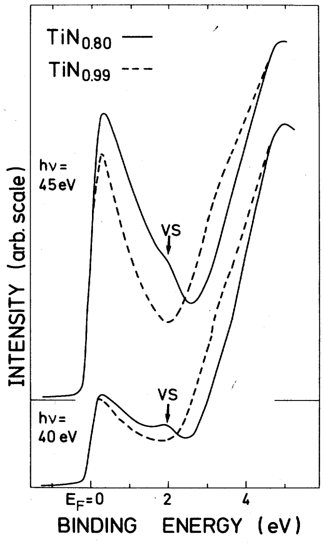

FIG. 5. Conduction-band spectra for TiN (broken line) and $TiN_{0.80}$ (solid line). The vacancy state is indicated by VS.

B. ZrN and $ZrN_{0.82}$

The results for ZrN and $ZrN_{0.82}$ were qualitatively similar to the corresponding results for TiN and $TiN_{0.80}$. A resonant enhancement of the $4d$ states occurs at 32 eV, which again is at a significantly higher energy than the Zr $4p$ binding energy of 27.9 eV.[1] In this section we will focus on the differences between the Zr nitrides and the Ti nitrides.

Spectra for both ZrN and $ZrN_{0.82}$ are shown at photon energies around the resonance in Fig. 6. The vacancy state seen for the nonstoichiometric titanium nitride is not as obvious in the zirconium case. A weak shoulder can be seen in the $ZrN_{0.82}$ spectra for $h\nu=50$ eV but is not evident at the other photon energies in this range. This difference between the two materials is consistent with the earlier XPS work[1] with $h\nu=1487$ eV, which revealed a distinct shoulder for $ZrN_{0.82}$ compared with a well-defined peak for $TiN_{0.80}$. A vacancy state had been seen earlier by Höchst *et al.*[18] in NbC and in calculations for nonstoichiometric NbC and VN.[19,20] It thus appears that the existence of occupied vacancy states in the refractory carbides and nitrides is a fairly common phenomenon.

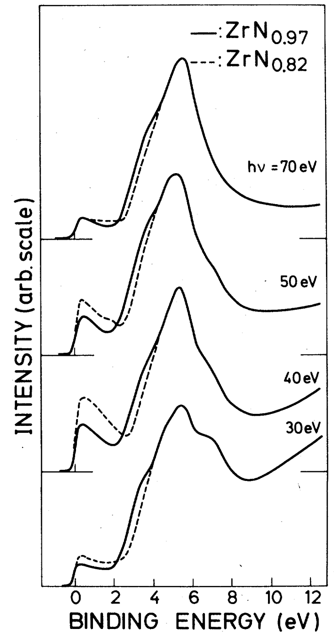

FIG. 6. Spectra for ZrN and $ZrN_{0.82}$ in the region near the resonance. The spectra have been normalized to the highest point of the valence band.

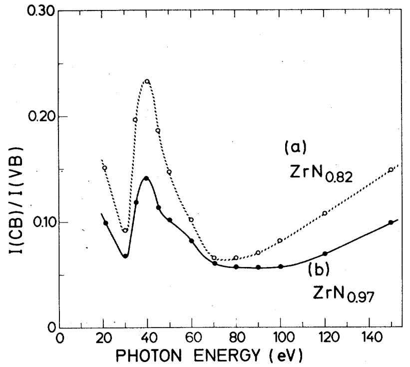

FIG. 7. Ratio of the conduction-band intensity to that of the valence band as a function of photon energy for ZrN and $ZrN_{0.82}$.

The ratio of the area under the conduction-band peak to that under the valence band is shown in Fig. 7 as a function of photon energy. A strong onset is seen at 32 eV but, in contrast to the titanium nitrides (Fig. 4), no other features occur in the photon-energy range up to 150 eV.

IV. CONCLUSIONS AND SUMMARY

Strong resonance effects due to super Coster-Kronig transitions were seen in TiN, $TiN_{0.80}$, ZrN, and $ZrN_{0.82}$. The main resonance occurred at photon energies significantly greater than the binding energies of the Ti $3p$ and Zr $4p$ levels but it is clearly related to the p-d transition. Several explanations exist for the discrepancy. The occurrence of a peak in the unoccupied density of states about 10 eV above the Fermi energy in the case of TiN is one possibility. The partial density of states calculated for TiN by Neckel *et al.*,[2] however, shows a significant $3d$ density of states immediately above the Fermi energy and one would still except a resonance as the photon energy reached the $3p$ binding energy. The simple onset behavior seen in Fig. 2 seems to rule out such a double threshold. An explanation based on variation of the exchange integral as the number of d electrons decrease below five has been given by Bertel *et al.*,[13] but no quantitative data has been presented. A third alternative is that the relaxation energy for the core hole is different in the photoemission case and the optical absorption/resonance case. The choice between these alternatives and other possibilities requires quantitative calculation and is beyond the scope of this paper. Nontheless, these resonance effects, which pick out the Ti $3d$ and Zr $4d$ states, unambiguously identify the atomic character of the occupied electron states in the region near the Fermi energy. In agreement with the partial density of states calculated for TiN by Neckel *et al.*,[2] the conduction-band peak is largely d-like and the valence band contains a mixture of transition-metal d and nitrogen p states.

The vacancy state[1,17] occurring at 2 eV below the Fermi energy in nonstoichiometric TiN_x and ZrN_x was found to exhibit no observable resonant behavior. This is a strong indication that the vacancy state has little d character. We have not observed the surface state seen by Johansson *et al.*[5] and Johansson and Callenas[6] on the (001) surface of single crystal $\mathrm{TiN}_{0.83}$.

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

[2] A. Neckel, P. Rastle, R. Eibler, P. Weinberger, and K. Schwartz, J. Phys. C **9**, 579 (1976).

[3] J. Klima, Czech. J. Phys. B **30**, 905 (1980).

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

[5] L. I. Johansson, A. Callenas, P. M. Stefan, A. N. Christensen, and K. Schwartz, Phys. Rev. B **24**, 1883 (1981).

[6] L. I. Johansson and A. Callenas, Solid State Commun. **42**, 299 (1982).

[7] J. E. Inglesfield, A. Callenas, and L. I. Johansson, Solid State Commun. **44**, 1321 (1982).

[8] U. Fano, Phys. Rev. B **124**, 1866 (1961).

[9] K. Schwartz, J. Phys. C **8**, 809 (1975).

[10] S. J. Oh, J. W. Allen, I. Lindau, and J. C. Mikkelson, Phys. Rev. B **26**, 4845 (1982).

[11] S. Shin, S. Suga, M. Taniguchi, H. Kanzaki, S. Shibuya, and T. Yamiguchi, J. Phys. Soc. Jpn. **51**, 906 (1982).

[12] See for example the compilation in *Photoemission in Solids I. General Principles,* edited by M. Cardona and L. Ley (Springer, Berlin, 1978).

[13] E. Bertel, R. Stockbauer, and T. E. Madey, Phys. Rev. B **27**, 1939 (1982).

[14] J. B. Mann, Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico, Report No. LA-3690, 1967 (unpublished).

[15] S. M. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Relat. Phenom. 21, 285 (1981). Data for C $2p$ and O $2p$ were used for an estimation of the cross section for N $2p$ and the value for Ti was taken from the calculation for Ni $3d^8$ and adjusted for Ti $3d^2$.

[16] L. I. Johansson, P. M. Stefan, M. L. Shek, and A. N. Christensen, Phys. Rev. B **22**, 1032 (1980).

[17] H. Höchst, R. D. Bringans, and R. L. Johnson, Ann. Israel Phys. Soc. **6**, 336 (1983).

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

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

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