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TiC(100) surface relaxation studied with low-energy electron diffraction intensity analysis

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The atomic structure of TiC(100) was determined precisely by low-energy electron diffraction intensity analysis. The surface atomic structure is relaxed; the topmost C atoms are displaced outward and Ti atoms inward with respect to the truncated bulk atomic positions. The results agree qualitatively with earlier theoretical work [D. L. Price, J. M. Wills, and B. R. Cooper, Phys. Rev. Lett. **77**, 3375 (1996)] and quantitatively with the latest theoretical results based on the first-principles molecular dynamics method [K. Kobayashi, Jpn. J. Appl. Phys., Part 1 **39**, 4311 (2000)].

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I. INTRODUCTION

Surface crystallography plays the same fundamental role in surface science as bulk crystallography has played so successfully in solid-state physics and chemistry. Atomic-scale structure is one of the most important aspects in understanding the behavior of surfaces in such widely diverse fields as heterogeneous catalysis, microelectronics, adhesion, lubrication, corrosion, coatings, and solid-solid and solid-liquid interfaces.

Refractory metal carbides exhibit interesting physical properties such as extremely high melting point, high hardness, high electrical conductivity, and superconductivity.[1] Recently, their surface properties have attracted considerable attention because of their use as catalytic materials for the hydrogenation of benzene, ethylene, and carbon monoxide, decomposition of methanol, etc.,[2–5] and also for electrocatalytic reactions.[6,7] In contrast to the substantial accumulation of data on transition metal surfaces, including theoretical work on the surface atomic structure, however, limited information is available on the atomic structure of the well-defined surfaces of transition metal carbides.

Transition metal carbides (TMC's) including TiC have the rock-salt crystal structure. The (100) surfaces exhibit (1×1) structures with equal numbers of metal and C atoms. Each C atom is situated at the center of a square net of metal atoms. They have been studied both theoretically[8–11] and experimentally.[12–15]

Detailed low-energy electron diffraction (LEED) I-V analyses were performed for two stoichiometric surfaces TaC(100) and HfC(100) by Gruzalski and co-workers.[14,15] They determined a rippled structure in the first and second layers; carbon atoms are displaced outward and metal atoms inward. The amplitude of the rippled structure for TaC agrees well with ones found by two theoretical calculations, a full-potential linear muffin tin orbital (LMTO) electronic structure calculation[11] and a first-principles molecular dynamics (FPMD) determination.[10] These values seem reasonable, considering force-constant changes.

For TiC some atomic structures have been proposed from the theoretical point of view. A simple d-p tight-binding model predicts inward relaxation for the surface C and outward relaxation for Ti.[9] On the contrary, LMTO and FPMD calculations predict outward relaxation for the surface C and inward relaxation for Ti.[8,10] One experimental report, by low-energy ion scattering (LEIS), $|r|<0.1$, does not have high enough accuracy to determine the correct positions of Ti and C.

Experimental evidence indicating surface relaxation on TiC(100) has been found in surface phonons. Changes in the chemical bonding near this surface were detected in the analysis of surface force constants. Above the bulk optical phonon bands, surface phonons were found with a polarization vertical to the surface, of which the vibrational amplitudes are located at the carbon atoms in the second outermost layer. To explain the appearance of these modes, the authors introduced changes in the force constants near the surface. Concerning the TiC(100) surface, the force constant between the first-layer Ti and the second-layer C should increase by 20%, while the force constant between the first-layer C and the second-layer Ti atoms decreased by 5% (Table I). The data strongly suggest a rippled relaxation of the surface; the carbon atoms are displaced outward and the Ti atoms inward in the topmost layer.[13]

In this paper, we report the surface atomic structure of TiC(100) determined precisely by a low-energy electron diffraction intensity analysis, which is one of the most reliable techniques for determining overlayer structures. The result clearly shows a rippled structure, of which the amplitude is 0.14 Å. It is in perfect agreement with the latest calculated one of 0.14 Å.[10]

II. EXPERIMENTAL AND CALCULATIONAL PROCEDURES

A single crystal of $TiC_{0.955}$ was grown by the floating-zone method[16] and cut into disks parallel to the (100) plane of ~1 mm thickness by spark erosion, and then one face was

TABLE I. Force-constant changes (in percent) between the topmost layer and the second layer of several TMC (100) surfaces. Here, $1M$ means the topmost-layer metal atom, $2M$ the second-layer metal atom, 1C the topmost-layer carbon atom, and 2C the second-layer carbon atom (Ref. 13).

Type of force constant	Compound				
	TiC	ZrC	HfC	NbC	TaC
$F(1M\text{-}2\mathrm{C})$	20	20	20	50	48
$F(1M\text{-}2M)$	18	5	50	0	0
$F(1\mathrm{C}\text{-}2M)$	−5	−24	−50	−20	−45

polished mechanically to a mirrorlike finish. The experiment was carried out in an ultrahigh-vacuum chamber equipped with four-grid LEED optics, an x-ray/ultraviolet photoemission spectroscopy (XPS/UPS) system, and a gas inlet. The base pressure of the UHV chamber was $\sim 1\times10^{-8}$ Pa. The surface was cleaned by flash heating up to about 1400 °C. Prior to measurements the cleanliness of the surface was confirmed using XPS. The clean surface shows sharp (1×1) LEED spot on a low background.

The LEED spot intensities were measured with a high-sensitivity chilled charge-coupled device camera connected to a personal computer. The intensities of four different spots at (1,0), (1,1), (2,0), and (2,1) were measured versus the electron energy from 50 to 300 eV. The final I-V curve for each spot was obtained by averaging the curves for symmetrically equivalent spots.

By using the same procedure, we have already detected a rippled structure of hexagonal BN on Ni(111), which has also been confirmed by x-ray photoelectron diffraction.[17]

In order to determine the surface crystallography, detailed comparisons were performed using a perturbation method. The surface region was conceptually divided into layers parallel to the surface, with each layer being a composite of a lattice of Ti atoms and a lattice of C atoms. Eight phase shifts were used to calculate the atomic scattering ($l_{\max}=7$). The attenuation due to thermal vibrations was modeled using a Debye-Waller formalism with different Debye temperatures for atoms on the surface and the bulk, $\theta_{\mathrm{sur}}=450$ and $\theta_{\mathrm{bulk}}=910$ K. The beam attenuation due to inelastic scattering was modeled by an optical potential where the imaginary component was 3.5 eV. The I-V spectra were calculated for a variety of models in which the interplanar spacings for the Ti and C sublattices were varied for layers near the surface. Since the LEED pattern is (1×1), no lateral displacements of the surface atoms were acceptable.

The calculated and measured I-V spectra were compared using the Pendry reliability factor R_P.[18] From the Pendry R factor for each structure, we have evaluated the atomic structure of the first two layers of TiC(100).

III. RESULTS AND DISCUSSION

The spacings between the C and Ti atoms in the first and second layers were adjusted systematically with optimization schemes. The best agreement with $R_P=0.19$ was obtained for a model with the following relaxations: the distance between the topmost carbon and the second-layer Ti atoms $d_{1\mathrm{C}\text{-}2\mathrm{Ti}}=2.25$ Å, $d_{1\mathrm{Ti}\text{-}2\mathrm{C}}=2.14$ Å, $d_{2\mathrm{Ti}\text{-}3\mathrm{C}}=2.19$ Å, $d_{2\mathrm{C}\text{-}3\mathrm{Ti}}=2.15$ Å, $r_1=0.14$ Å, and $r_2=0.03$ Å. The experimental accuracy was ±0.03 Å. The side view of the structure is depicted in Fig. 1, and the I-V curves in Fig. 2.

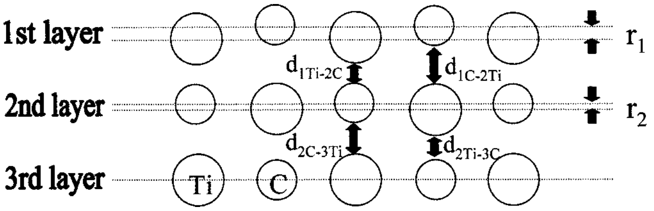

FIG. 1. The side view of the best-agreement structure of TiC(100) with the minimum at $R_P=0.19$. The bulk interlayer spacings $d_{\mathrm{bulk}}=2.1635$ Å.

The constant-R_P contour plot as a function of $d_{1\mathrm{C}\text{-}2\mathrm{Ti}}$ and $d_{1\mathrm{Ti}\text{-}2\mathrm{C}}$ shows that the best agreement is for $d_{1\mathrm{C}\text{-}2\mathrm{Ti}}=2.25$ Å and $d_{1\mathrm{Ti}\text{-}2\mathrm{C}}=2.14$ Å (Fig. 3). Below the second layer the atoms are fixed, and Ti and C in the first layer were moved independently. The R factors become worse as the lines move outward. The rippled structure of the surface reduces the R factor to 0.19 from that of the truncated bulk structure (0.38). Note that the contours are elliptical. If they were circular, then the structure analysis would be equally sensitive to both of two atomic distances $d_{1\mathrm{C}\text{-}2\mathrm{Ti}}$ and $d_{1\mathrm{Ti}\text{-}2\mathrm{C}}$. As the contours are distorted, the R factor is sensitive to $d_{1\mathrm{Ti}\text{-}2\mathrm{C}}$ rather than $d_{1\mathrm{C}\text{-}2\mathrm{Ti}}$. This is consistent with the larger scattering factor of Ti than that of C.

In Table II, our results are compared with three theoretical values calculated on the basis of LMTO,[8] tight-binding,[9] and FPMD methods.[10] The directions of the observed atomic displacement in the surface relaxation are the same as the theoretical results obtained by LMTO and FPMD calculations, but different from that of the tight-binding method. Moreover, the FPMD calculation predicted the same ripple amplitude as the experimental one, 0.14 Å; the FPMD calculation provides perfect agreement with the present results.

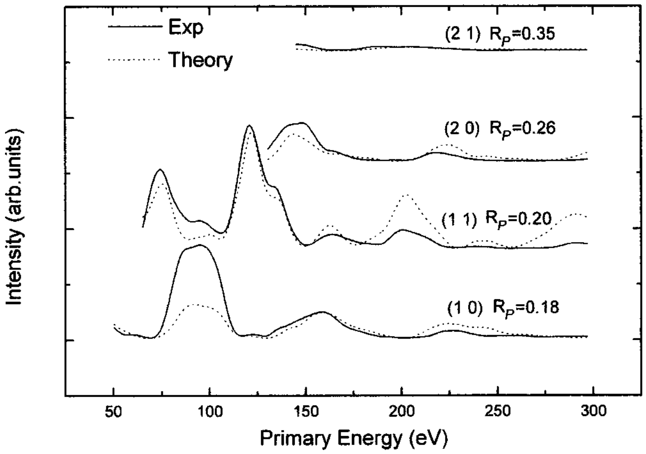

FIG. 2. Comparison of the measured I-V curves (exp) with calculated curves (theory) for four diffraction spots on the TiC(100) surface.

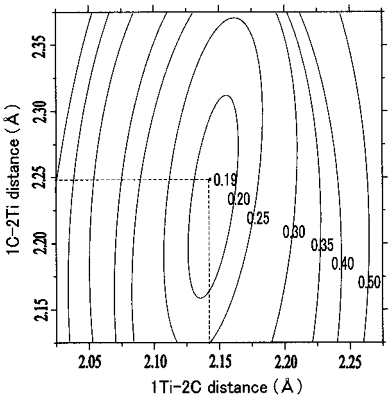

FIG. 3. The constant-R_P contour plot as a function of the first interplanar spacings.

In addition, the FPMD results explain two other experimental facts: the surface force-constant change and the surface active points for reaction.[10] According to the theoretical results, ripple relaxation increases the work function, because the net electrons flow is from the crystal to the vacuum side owing to the ripple formation. The FPMD calculation also shows that the direction of the partial electron flow around the topmost Ti is opposite to that around the topmost carbon. Electrons around the topmost Ti atoms move from the vacuum to the crystal, while electrons around the topmost carbon atoms move in the opposite direction, from the crystal to the vacuum. This explains well the force-constant changes observed in surface phonon spectroscopy: an increase in the force constant between the topmost Ti and the second-layer carbon, and a decrease between the topmost C and the second-layer Ti.[10]

The surface relaxation of TMC's has great importance in catalytic reactions. TiC has a similar catalytic function to Pt. Two experimental studies by LEIS spectroscopy and by UPS suggest strongly that oxygen atoms are adsorbed on the topmost carbon atoms, not the Ti atoms.[19,20] These experimental results show that the carbon atoms of TiC(100) play an important role in the catalytic process. Electrons near the Fermi energy localize in the vicinity of carbon atoms, and these electrons presumably make a contribution to adsorption. These views are also supported by the FPMD calculation.[10] The surface electronic state and the wave function are changed, and the surface becomes stable owing to relaxation. As a result, carbon atoms become active.

TABLE II. The ripple amplitude r_1 (in Å) of TMC (100) surfaces.

Method	TiC	ZrC	HfC	NbC	TaC
LEED I-V (present, Refs. 4,15)	0.14		0.11	0.16	0.2
FPMD (pc) (Ref. 10)	0.14	0.12	0.13	0.22	0.23
FPMD (np) (Ref. 10)	0.14	0.12	0.09	0.23	0.23
LMTO (Refs. 8,11)	0.05				0.21
Tight binding (Ref. 9)	-0.07				0.12
LEIS (Ref. 12)	$\|r\|<0.1$				

IV. SUMMARY

The detailed rippled structure of TiC(100) determined by tensor LEED analysis agrees with both the calculations based on FPMD and the results of surface phonon experiments. The surface phonon dispersions are also strongly correlated with the surface structure, which explains the dispersion and also the important role of carbon atoms in the surface catalytic process.

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