Scanning tunneling microscopy studies of niobium carbide (100) and (110) surfaces

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Received 4 September 1995; accepted for publication 3 May 1996

Abstract

Scanning tunneling microscopy (STM) studies were conducted on the surfaces of NbC 0.75(100) and NbC 0.865(110) single crystals after in situ cleaning treatments of sputtering and annealing cycles. STM images show atom-resolved structures of both surfaces. On NbC 0.75(100), localized areas of a square (1 × 1) structure were observed, together with regions of hexagonal structure, indicative of a coexisting surface phase, possibly that of Nb 4 C 3−x. On the NbC 0.865(110) surface, a ridge-and-valley grating structure consisting of both (4 × 1) and (5 × 1) geometries was observed over large areas. The nanometer-scale faceting phenomenon may be common to the (110) surfaces of most transition-metal carbides.

Keywords: Carbides; Low index single crystal surfaces; Scanning tunneling microscopy; Surface structure, morphology, roughness, and topography

1. Introduction

Transition metal carbides have been of considerable technological interest in the past three decades because of their unusual combination of physical properties, i.e., high melting points, good electrical conductivity, and extreme hardness. They are almost always nonstoichiometric, containing vacancies in the carbon lattice sites with a range of compositions [1,2]. In the present report, the carbides of interest are the (100) and (110) surfaces of single-crystal NbC. These carbides possess a single-crystal structure of the NaCl type as shown in Fig. 1. The lattice parameter of pure NbC varies with composition given empirically by the equation

\[ a_0 = 4.09847 + 0.71820(\text{C/Nb}) - 0.34570(\text{C/Nb})^2, \]

where C/Nb is the atom ratio [1]. For the crystals studied in the present work NbC 0.75(100) and NbC 0.865(110), the lattice parameters according to Eq. (1) are 4.44 and 4.46 Å respectively, which correspond to the length of an edge of the cube shown in Fig. 1. For the purpose of this work, we take the closest Nb–Nb and C–C distance as \( \sim 4.45\sqrt{2} \), or \( \sim 3.14 \) Å. The ideal bulk-terminated (1 × 1) surfaces of (100) and (110) are depicted schematically in Fig. 2.

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As far as we can tell, there have not been any detailed studies on the surface structures of NbC(100) and (110). On the NbC(100) surface, researchers using angle-resolved photoemission spectroscopy (ARPES) and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) to conduct electronic structure and gas adsorption studies have reported the observation of a (1 x 1) low-energy electron diffraction (LEED) pattern after annealing the surface at 1100–1200°C [3,4] and at 1500–1600°C [5–8]. Detailed studies of the structures of (100) surfaces of related carbides of TaC and HfC have been reported by researchers from the Oak Ridge National Laboratory using LEED, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) [9,10]. Although the LEED patterns were (1 x 1), detailed LEED I–V analyses showed that on both surfaces, carbon atoms were displaced outward and metal atoms inward, giving rise to a rippled reconstruction [9,10]. There have been no reports of any investigation conducted on the NbC(110) surface. However, Zuo et al. [11,12] have studied the surface structure of TaC(110) using LEED and scanning tunneling microscopy (STM) and they observed unidirectional alternating (100) and (010) facets, resembling a ridge-and-valley grating structure on the surface where (110) terraces were completely absent. Zuo et al. [11,12] also reported observing a similar LEED pattern for the surface of HfC(110), leading them to suggest that such faceting behavior might be expected on other transition-metal carbide (110) surfaces. Zaima et al. [13] reported the formation of microscopic (310) facets on TiC(110), but no details were provided. A recent review of transition metal carbide and nitride surfaces has been given by Johansson [14].

In the present work, we report the studies of the NbC(100) and (110) surfaces using a scanning
tunneling microscope (STM) in an ultrahigh vacuum (UHV) environment. Notwithstanding the large number of STM studies conducted on the surfaces of semiconductors and metals over the past decade, the only STM studies on transition metal carbide surfaces were the work on TaC(110) by Zuo et al. [11,12] mentioned earlier, and that by Hammar et al. [15] on VC_{0.8}(111). This apparent lack of interest is probably due to the limited availability of single-crystal samples of these carbides. A particular objective of the present STM investigation was to determine whether or not the nanometer-scale faceting would also occur on the NbC(110) surface, as predicted by Zuo et al. [11,12].

2. Experimental

The NbC_{1-x} single crystals, where 1-x = 0.750 for the (100) and 0.865 for the (110) orientation, were grown by the floating zone method. The crystals were cut by spark erosion into 2 mm thick disks and were polished mechanically. Details of preparation and chemical composition of these crystals were given previously by Ledbetter et al. [16].

The UHV-STM apparatus consists of two inter-connected chambers, one for sample preparation, and the other housing the STM. The NbC_{0.75}(100) and NbC_{0.865}(110) samples were each introduced separately into the preparation chamber to undergo sputtering and annealing cycles to produce a clean and ordered surface prior to STM imaging. The surface was sputtered by 1 keV Ar^+ ions at an incident angle of 67° with an ion current of 1.5 μA for 10-min periods. At the end of each sputtering period, the sample was annealed at temperatures ranging from 1000–1180°C, also for 10-min periods. Although workers from Japan [3,4] reported an ordered (1 × 1) LEED pattern for the NbC(100) surface after annealing at the temperature range 1100–1200°C, it would be desirable to anneal at a higher temperature to ensure cleanliness of the surface. However, because of the heavy masses of the NbC_{1-x} crystals, 1.30 g for the (100) and 1.04 g for the (110) respectively, combined with the 10 g mass of the Mo sample holder, the electron-beam heater in our STM was unable to reach higher annealing temperatures.

After the sputtering and annealing cycles, we did not obtain an LEED pattern for the NbC_{0.75}(100) surface, contrary to the reports of Kojima et al. [3] and Edamoto et al. [4]. Auger electron spectroscopy (AES) scans of the surface showed small traces of oxygen. On the NbC_{0.865}(110), however, an ordered LEED pattern was observed with spots elongated in the (1,0) direction on either side of the (1 × 1) spots i.e. the elongated spots could be a mixture of (4/5,0) and (3/4,0) spots, or (6/5,0) and (5/4,0) spots, indicative of coexisting reconstructions of (4 × 1) and (5 × 1). AES scans of the (110) surface showed no trace of oxygen.

After the cleaning treatment, the samples were individually transferred from the preparation chamber to the STM chamber. The pressure inside the STM chamber was below 1 × 10^{-10} mbar. Once the sample was mounted inside the STM, scanning was carried out with a gap voltage between 5 and 10 mV for atom-resolved images and ~ 100 mV for larger area scans, with negative bias on the sample and a tunneling current of ~ 1 nA. Similar to the STM experiments of Hammar et al. [15] on VC_{0.8}(111), the tunneling voltage and current settings were not critical, and a reversal of bias did not have any noticeable influence on the image.

3. Results and discussion

3.1. NbC_{0.75}(100)

The lack of any LEED pattern from the NbC_{0.75}(100) surface after the cleaning treatment indicated that the surface was not well ordered. The STM images tend to support such a finding. A large-area scan (1000 Å × 1000 Å), of the surface (Fig. 3) clearly shows terraces and steps, but the overall surface is rough, with a corrugation as high as ± 1 Å in places. There are also dark triangular pits on the terraces, suggesting a threefold symmetric surface. The height of the terrace steps and the depth of the triangular pits were both measured at
Fig. 3. 1000 Å × 1000 Å STM image of the NbC_{0.75}(100) surface, showing terraces and steps.

4.0 ± 0.5 Å. On certain localized regions of the surface, such as the 50 Å × 50 Å area shown in Fig. 4, atom-resolved STM images could be obtained. The bright spots form a square array with a spacing of 3.1 Å between nearest neighbors. This corresponds exactly to the (1 × 1) bulk-terminated surface shown in Fig. 2a, with only one of the atom-species present. It is likely that the Nb atoms were imaged in Fig. 4 because there are no vacancies among the bright spots. Since C is under-stoichiometric, we would expect to find ~25% vacancies among the bright spots if C atoms were imaged, unless of course the vacancies occur only in the bulk and not on the surface. It is also our general experience from STM studies on surface alloys that metal atoms appear bright and non-metal atoms appear dark, e.g. the Si atoms are dark in SiFe(100) and (110) surface alloys [17,18]. Moreover, our STM study of C-segregation on a Pt_{10}Ni_{90}(100) surface [19] showed that while the metal atoms appeared bright, the C atoms showed their presence in the form of a reduction of the apparent height of the neighboring metal atoms. Occasionally, under special tip conditions where chemical interaction between the foremost tip atom and the surface has occurred, the C atoms would become visible [19].

XPS studies on the (100) surface of TaC_{x} by Grzulsaki and Zehner [20] have provided evidence of charge transfer from C atoms to Ta atoms as x decreases. Such a charge-transfer phenomenon can account for a change in the bright-and-dark contrast in STM images when the sample bias is changed from positive (i.e. sampling empty states) to negative (i.e. sampling filled states). A contrast reversal of this nature as a result of charge transfer has been identified by us [21] in a previous STM study of a β-SiC(111) surface covered by a graphite adlayer. By this reasoning, charge transfer on the NbC_{1-x}(100) surface could possibly lead to a shift in registry by half of the lattice constant of the bright spots shown in Fig. 4 when the sample bias is reversed, in much the same way as that observed on the GaAs(110) surface [22]. However, this was not observed by us.

On other localized areas of the (100) surface, STM images show bright spots arranged in a hexagonal pattern with nearest-neighbor distances of 2.5 Å. Such an image is shown in Fig. 5. This hexagonal surface phase coexists with the (1 × 1) phase shown in Fig. 4. The triangular pits on the terraces in Fig. 3 reflect the symmetry of the hexagonal phase on the (100) surface over larger areas. The hexagonal structure could be the result of a transitional Nb_{3}C_{3-x} phase below 1800°C between 33 and 42 at% of C in the NbC phase diagram [23]. The NbC_{0.75} has 42.86% carbon. The cleaning treatment of sputtering and annealing cycles could conceivably lower the C content into the transitional phase. Carbon-to-niobium peak ratios of AES scans taken after each sputtering and

Fig. 4. 50 Å × 50 Å STM image of the NbC_{0.75}(100) surface, showing a square (1 × 1) geometry of the atoms. The distance between the two nearest atoms is 3.1 Å, and the corrugation along a line joining nearest neighbors is ~0.1 Å.
annealing cycles indicated a diminishing trend of C, which may have been enough to change the C content to <42% on the surface. Although the exact structure of the transitional Nb₄C₃-x phase has not been determined [23], it could possibly account for the hexagonal structure observed in Fig. 5 since the Nb₂C (i.e. x = 1) phase at 33 at% C is known to have an ordered hexagonal form [23].

3.2. NbCo.₈₆₅(110)

STM images of the NbCo.₈₆₅(110) surface after the cleaning treatment show a ridge-and-valley grating structure, covering areas as large as 1000 Å x 1000 Å similar to that observed by Zuo et al. [11,12] for the TaC(110) surface. A typical STM image of this grating structure is shown in Fig. 6. A high-resolution image of the grating structure is displayed in Fig. 7. The distance between two adjacent bright spots on the same row in Fig. 7 is 4.5 Å. Thus, according to Fig. 2b, the spacing between two atom-rows on the same plane should be multiples of 3.14 Å, giving a (n x 1) reconstruction on the surface. We have labeled the atom rows in Fig. 7 with the numbers 1, 2 and 3, indicating that the rows lie on the first, second and third atomic layers respectively. The height difference between two layers is 1.56 Å, in agreement with that shown in Fig. 2c. A grid is drawn in Fig. 7 with a grid size of 4.5 Å in the [001] direction, i.e. along the atom rows, and 3.1 Å in the [110] direction, i.e. across the atom rows. We immediately see that atom rows in the same layer are n a apart, where a = 3.1 Å, while atom-rows in different layers are (n+1/2)a apart. For rows located in the same atomic layer, we find n = 4 or 5, thus confirming the LEED observations of the coexistence of (4 x 1) and (5 x 1) reconstructions. The distance between rows located in layers 1 and 2 is 4.5a or 3.5a, as determined by the grid over two such pairs of rows in Fig. 6.

A missing-row model similar to that proposed by Zuo et al. [11,12] is given in Fig. 8 to explain our observations in Fig. 7, where the atom rows...
Fig. 7. Atom-resolved 150 Å × 150 Å image of the (n × 1) grating structure. The distance between two adjacent atoms is 4.5 Å, and thus the atom rows or “ridges” lie along the [001] direction. The numbers 1, 2 and 3 indicate rows on the first, second and third atomic layers respectively. A grid is drawn with a size of 4.5 Å along the atom-rows and 3.1 Å across the rows. The image has been contrast-enhanced in the region of the grid for better visibility of the atomic corrugation.

run along the [001] direction, perpendicular to the plane of the paper in Fig. 8. Atom rows on the same plane can have a spacing of 4a or 5a depending on the depth of the valleys. Atom rows in different planes with a single atom-layer height difference have a spacing of 4.5a, but can also vary depending on the valley depth. Single line-scans taken across the atom rows in Figs. 6 and 7 show valleys with depths varying from 1.5 to 3.5 Å, much less than the depths indicated in Fig. 8. The apparent gentle ripple of the surface is probably the result of the convolution of the tip geometry and the ridge-and-valley structure. We did not observe the sharp bottoms of the valleys attributed to quick withdrawal of the tip by Zuo et al. [11,12]. Although we cannot deduce the orientation of the facets from our line-scan profiles, it is likely that the valley walls are (100) and (010) facets, as labeled in Fig. 8, similar to those reported by Zuo et al. [11,12], since low-index facets are generally more favorable.

The (6 × 1) ridge-and-valley structure on TaC(110) [11,12] together with the similar (4 × 1) and (5 × 1) structures on NbC_{0.865}(110) observed here, suggest that the nanometer-scale faceting phenomenon may be quite universal. Supporting evidence is provided by the high-resolution LEED studies of Zuo and Zehner [24] on the TaC(310) surface, where nine atom-row (100) facets with

Fig. 8. Schematic model showing the ridges and their spacings. Each ridge or atom-row, containing both Nb and C atoms, lies perpendicular to the paper in the [001] direction. a = 3.13 Å and t = 1.56 Å as defined in Fig. 2b and Fig. 2c. The facet directions of [100] and [010] are also shown. The open and filled circles represent Nb and C atoms respectively.
triple-height (010) steps were reported. In addition, we have observed (3 x 1) and (4 x 1) ridge-and-valley structures on the VC(110) surface with STM [25]. All these observations point to the fact that the instability of planes other than the (100) may be common to many, if not all, transition-metal carbides.

The question remains whether the bright rows in Fig. 6 and the bright spots in Fig. 7 are due to Nb or C atoms. From Fig. 7 the measured spacing of 4.5 Å between bright spots tells us that they are either Nb or C atoms, but not both. It is tempting to suggest that they are due to C atoms from the observation that some of the rows terminate abruptly (Fig. 6), indicative perhaps of rows of missing C atoms in the non-stoichiometric NbC_{0.865}. However, a careful examination of Fig. 6 and other such images of the grating structure reveals that too high a vacancy concentration would result if terminating rows were the cause. It is conceivable that the terminating rows are due to a slight miscut of the surface or are the result of mechanical polishing of the surface. So it is difficult to tell from Figs. 6 and 7 whether the Nb or C atom was imaged by the STM on the (110) surface. We have, however, proposed earlier from Fig. 4 for the (100) surface that Nb atoms were imaged by the STM. Apart from the non-detection of charge transfer, existing experimental evidence appears to suggest that the atom-resolved STM images are due to metal atoms.

4. Conclusions

Our STM studies show the existence of small localized regions of (1 x 1) bulk-terminated structure on the NbC_{0.75}(100) surface. Other ordered regions of the (100) surface contain a hexagonal structure which could be the result of a transitional phase [23] when the C content falls below 42 at%. Since only ~5% of the (100) surface provided atom-resolved images, further experimentation at higher annealing temperatures to produce a cleaner surface would be very beneficial. On the NbC_{0.865}(110) surface, in spite of the low annealing temperatures (maximum 1150°C), we observed a ridge-and-valley grating structure throughout the surface very similar to that observed previously for TaC(110) [11,12]. A missing-row model (Fig. 8) similar to that of Zuo et al. [11,12] was proposed to explain the observed (4 x 1) and (5 x 1) structures. The nanometer-scale faceting phenomena may be universal for all transition-metal carbide (110) surfaces.

Acknowledgements

R.M.T. thanks the College of William and Mary for the award of a James Monroe Scholarship to carry out this work at the Technische Universität Wien. M.S., C.N. and P.V. were supported by the Fonds zur Förderung der Wissenschaftlichen Forschung (Austrian Science Foundation). I.S.T.T. was supported by the US Army Research Office under grant number DAAL-03-92-G-0038.

References


