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Surface Science 584 (2005) 237–244
SURFACE SCIENCE
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Electronic structure of the Ti suboxide layer formed on a TiC(100) surface: Angle-resolved photoemission study

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Received 17 December 2004; accepted for publication 25 March 2005
Available online 20 April 2005

Abstract

Angle-resolved photoemission spectroscopy (ARPES) utilizing synchrotron radiation has been used to study the electronic structure of a TiO-like layer formed on a TiC(100) surface. When the TiC(100) surface exposed to 500 L of O_2 is heated at 1000 °C, a TiO-like layer with the thickness of 1.3–2.0 Å is formed on the surface. ARPES measurements show that the Ti 3d band and O 2p band are formed in the TiO-like layer at around the Fermi level and at 6–7 eV, respectively. Both bands show clear dispersions along both $\langle 100 \rangle$ ($\overline{\Gamma}\overline{M}$) and $\langle 011 \rangle$ ($\overline{\Gamma}\overline{X}$) symmetry directions of TiC(100), and the dispersive features are compatible with a (1×1) periodicity of TiC(100). These results are compatible with the model that the oxide layer is a well ordered TiO(100) film which is epitaxially grown on the TiC(100) surface.

Keywords: Angle-resolved photoemission; Surface electronic phenomena; Carbides; Low index single crystal surfaces

1. Introduction

The early transition metal carbides (TMCs) have attracted much attention because they have an interesting combination of useful properties such as extreme hardness, a high melting point and metallic conductivity [1]. In practical applications, they have been found to be useful as stable field electron emitters [2]. It is also known that a stable emission current is available from these TMCs particularly when their surfaces are oxidized [3], thus the oxidation process and its effect on the electronic structure of the TMC surfaces are of particular interest. In addition, the TMCs have recently been shown to form an interesting new group of catalysts [4–8]; for example, they have been found to exhibit high catalytic activities

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doi:10.1016/j.susc.2005.03.058

for the reactions involving C–H bond transformation such as dehydrogenation and hydrogenation reactions [6–8]. It has been reported that the catalytic activities of the TMCs are often improved by slight oxidation of their surfaces [6–8], and thus the oxidation process of the TMC surfaces is of much interest also from a chemical viewpoint.

Recently we studied the oxidation process of TiC(1 0 0) using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), and found that a well-ordered suboxide (TiO)-like layer is formed on the TiC(1 0 0) surface when the surface covered with oxygen is heated at ~1000 °C [9,10]. It was also found that, when the surface is covered with the TiO-like layer, the work function is lowered from that of the TiC(1 0 0) surface by approximately 1.0 eV and the electronic density of states (DOS) around the Fermi level (E_F) is increased [9,10], both of which evidently contribute to the improvement of the field electron emission efficiency. The electronic states around E_F should be involved in many surface reactions, and thus the enhancement of DOS around E_F should have substantial effect on the surface reactivity. It seems that the oxidative treatment forming a suboxide layer is essential to reform the TMC surfaces. To explore further the functionality of the TiO-covered TiC(1 0 0) surface, it is important to elucidate the electronic structure of the TiO-like layer particularly in the vicinity of E_F. In this paper, we report the results of an angle-resolved photoemission spectroscopy (ARPES) study with synchrotron radiation for the valence electronic structure of the TiO-like layer formed on the TiC(1 0 0) surface.

2. Experimental

A $TiC_{0.96}$ single crystal was grown by the floating zone method at the National Institute for Materials Science [11]. The crystal was cut at an orientation of (1 0 0) by spark erosion into a disk of ~1 mm thickness, and subsequently polished mechanically. The sample was flashed repeatedly above 1500 °C in the vacuum chamber to remove surface contaminants. The surface thus obtained showed a sharp (1 × 1) LEED pattern but a small O 1s peak was observed in the XPS spectrum [9]. The temperature of the surface was monitored using a W-Re(3%)/W-Re(25%) thermocouple and an optical pyrometer.

The ARPES measurements using synchrotron radiation were performed on the Beam Line 11C of the Photon Factory, High Energy Accelerator Research Organization, where the light was dispersed by a Seya-Namioka monochromator. An electron energy analyzer of 180° hemispherical sector type with an acceptance angle of ±1° was used for the ARPES measurements. The total experimental resolution was estimated to be 0.15 eV at $h\nu = 20$ eV [12]. The base pressure in the vacuum system was 1.0×10^{-10} Torr.

In this paper, the incidence angle of the light (θ_i) and detection angle of the photoelectrons (θ_d) are given relative to the surface normal, and the coordinate system is chosen such that the z-axis is normal to the surface and the x- and y-axes coincide with the crystallographic ⟨1 0 0⟩ and ⟨0 1 1⟩ directions, respectively. The incidence light was linearly polarized in the incidence plane for all measurements. The spectra presented below are normalized by photon flux estimated from the photocurrent of the final stage mirror. All the spectra presented below were measured at 20–50 °C.

3. Results

First, we briefly summarize the oxidation process of TiC(1 0 0) elucidated by our previous investigations [9,10]. When a TiC(1 0 0) surface is exposed to O_2 at room temperature, the C atoms near the TiC(1 0 0) surface are depleted probably due to desorption as CO or CO_2 molecules, and the substrate's Ti atoms react with oxygen to form a disordered TiO_x ($1.5 < x < 2.0$) layer on the TiC(1 0 0) surface. As the surface exposed to O_2 is annealed at elevated temperatures, the TiO_x layer is reduced, and the TiO-like layer that produces a sharp (1 × 1) LEED pattern is formed upon heating at approximately 1000 °C. Details of the oxidation process of the TiC(1 0 0) surface has been discussed in our previous papers [9,10]. In the current study, the TiO-like layer is formed