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Atomically resolved interface structure between epitaxial TiN film and MgO substrate

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ABSTRACT

In this study, we used a high quality epitaxial TiN thin film grown on MgO (001) substrate for the investigation of the TiN/MgO interface structure which was characterized with scanning transmission electron microscopy (STEM) at atomic resolution. Analyses of high angle annular dark-field and annular bright-field STEM image contrast with X-ray energy dispersive spectroscopy maps show that a 2~4 nm diffuse interlayer of mixed compositions exists coherently between TiN and MgO with the same structure and across the interface the ionic bonding sequences are maintained without any interruption.

1. Introduction

TiN is one of the most important transition metal nitrides with cubic NaCl type structure has attracted intensive attention because of remarkably thermodynamic stability [1], excellent mechanical properties, low electrical resistivity [2] and distinctive gold color [3]. In the past, heteroepitaxially grown thin film has been widely used to study the basic properties of TiN as single crystal is not easily available. TiN and MgO of the same NaCl structure have very similar lattice constant (lattice parameter $a_{TiN} = 0.424$ nm [3] and $a_{MgO} = 0.421$ nm [4]) which gives small lattice mismatch (<1%), for which TiN film can be grown on MgO substrate with high-quality. It is known that the film/substrate interfaces with the bonding characteristics may have strong influence on many material properties such as thermal conductivities, adhesion, corrosion resistance, and resistivity, etc. Therefore, investigation of specific simple system of the TiN/MgO interfaces may provide detailed insight about the interfacial properties. Though the TiN/MgO interfaces have been previously studied [5–8], the interfacial structure is still far away from being completely understood. Recently, first-principle calculations based on the density-function theory have been applied to establish precise atomic and electronic structures of interfaces between TiN and MgO, suggesting that the interface with cation–anion bonding configurations (namely, Ti—O and Mg—N) is energetically favorable for TiN/MgO [9,10]. High resolution transmission electron microscopy (HRTEM) has been conventionally applied on studies of the interface. However, interpretation of the HRTEM image often encounters with difficulty from contrast reversal and variation due to the imaging conditions and specimen thickness, such that it may not unambiguously be certain about the exact atomic positions, even with image simulation. However, to understand atomistic bonding configurations across the interface, it is essential to know the image contrast corresponding with atoms. Recent development of spherical-aberration corrected scanning transmission electron microscopy (STEM) has shown robust image contrast at atomic resolution which simply image interpretation. The purpose of the present work is to investigate the TiN/MgO (001) interfacial structure by using of STEM HAADF (high-angle annular dark-field) and ABF (annular bright-field) imaging. Atomic resolution HAADF images provide a high-accuracy to identify atomic species as the atomic column height intensity, I, depends on atomic number, Z, approximately in a relation of $I \propto Z^n$ ($n = 1.5$–1.7). Though HAADF imaging leads to data that is much easier to interpret, the atoms of light elements in the presence of heavy atoms may be invisible even at high resolution. Nevertheless, ABF imaging at atomic resolution can clearly reveal both light and heavy atomic positions [11,12]. Since TiN/MgO is a simple system with different elements across the film/substrate interface, atomic resolution STEM imaging can reveal the interfacial characteristics in details.

2. Experimental

Epitaxial TiN thin films were grown on single-crystal MgO substrates by pulsed laser deposition with base pressure of 1.33×10^{-4} Pa. A 2-inch MgO (001) substrate was placed opposite to a 2-inch TiN target at a distance of 14 cm. Before TiN deposition, the MgO substrate was heat-treated at 800 °C in vacuum for 1 h to clean the surface, followed by TiN growth under the condition of a laser pulse repetition rate of 5 Hz, substrate temperature at 800 °C and growth time for 3 h. The crystallinities of the grown thin films were measured with high resolution

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X-Ray diffractometry. The full-width at half-maximum of (002) TiN X-ray rocking curve is about 60 arc sec, indicating that the TiN films deposited on MgO are of good quality.

Cross-sectional STEM specimens were prepared along ⟨110⟩ direction by tripod polishing method. Sandwich specimens were fabricated by gluing with Si dummy wafers at both sides of the specimen to protect the film from damage. A series of abrasive diamond papers were used for mechanical grinding and polishing in order to progressively reduce the roughness to about 0.5 μm and the thickness to 30–50 μm. Final electron transparency was obtained by ion milling using a precision ion polishing system (PIPS, Gatan Model 691) with double Ar-ion beams milled at an angle of 4–5° and acceleration voltage of 4–5 kV. The wedge shape of the specimen can be estimated from the HAADF image intensity which linearly increases with the specimen thickness, from which the thickness around the interface may be <50 nm for wedge angle <10°. As TiN and MgO have different sputtering properties which may result in thickness variation across the interface, the sandwich samples were evaluated with those prepared by focused ion beam (FIB) which had uniform thickness across the interface. FIB was carried out in an FEI Nova 200 system using a Ga ion beam with accelerating voltage from 30 to 5 kV and the corresponding current from 7 to 0.1 nA. For the final fine polishing process in FIB during which the accelerating voltage was reduced 5 kV, it might have damage on the surfaces of the TEM specimen but little effect on intermixing because of the protection of the Pt layer. The measured variation of the HAADF image intensity ratio of TiN/MgO has been evaluated for specimens prepared with both methods, and the results show the contrast cross the interface is almost the same, implying that the effect of thickness variation around the interfacial region on the image interpretation can be ignored.

All STEM image observations were performed in an aberration-corrected STEM microscope (JEOL JEM-ARM200F with a Schottky gun) at an acceleration voltage of 200 kV. For HAADF/ABF imaging condition, a probe size of 0.1 nm and a convergence semi-angle of 22 mrad were used. The collection semi-angles from the inner to outer ones for the HAADF and ABF imaging were 68–175 mrad and 10–17 mrad, respectively. X-ray energy-dispersive spectroscopy (EDS) was performed with the equipped Oxford Instrument MAX80 silicon-drift-detector (energy resolution ≤127 eV at Mn Kα and <56 eV at C Kα). Simulation of the HAADF and ABF images was performed by using the QSTEM software package which is based on a multislice method with the frozen phonon approximation [13].

3. Results and discussion

The cross-sectional HAADF image in Fig. 1(a) shows an overview of the TiN film and the MgO substrate with the interface. The distinctly sharp image contrast can easily identify the 80 nm thick TiN film in bright contrast and the MgO substrate in dark contrast. As a result, the high-resolution TEM (HRTEM) image can be taken at the interface as shown in Fig. 1(b). As expected, the HRTEM image clearly shows that TiN is in epitaxy with MgO from which the epitaxial relationship can be shown to be (001)TiN//(001)MgO and [110]TiN//[110]MgO. The filtered HRTEM image in Fig. 1(c) clearly shows that the TiN/MgO interface is almost fully coherent due to a small lattice mismatch ($\delta = 0.7\%$) between MgO and TiN. However, the HRTEM image reveals no information about the chemical bonding across the interface. To further understand the chemistry at the interface, STEM-HAADF image observations were performed with atomic resolution. Fig. 2 shows a typical atomic-resolution HAADF image around the TiN/MgO interfacial region which reveals the distinct Z-contrast of the film and substrate due to the difference in atomic number [Z(Ti) = 22, Z(Mg) = 12, Z(O) = 8 and Z(N) = 7]. It is observed that the image of TiN film on top and MgO substrate on bottom is seen in bright and dark contrast, respectively; in addition that contrast variation exists in the region of 2–4 nm width between TiN and MgO. From the line profiles of framed blocks A and

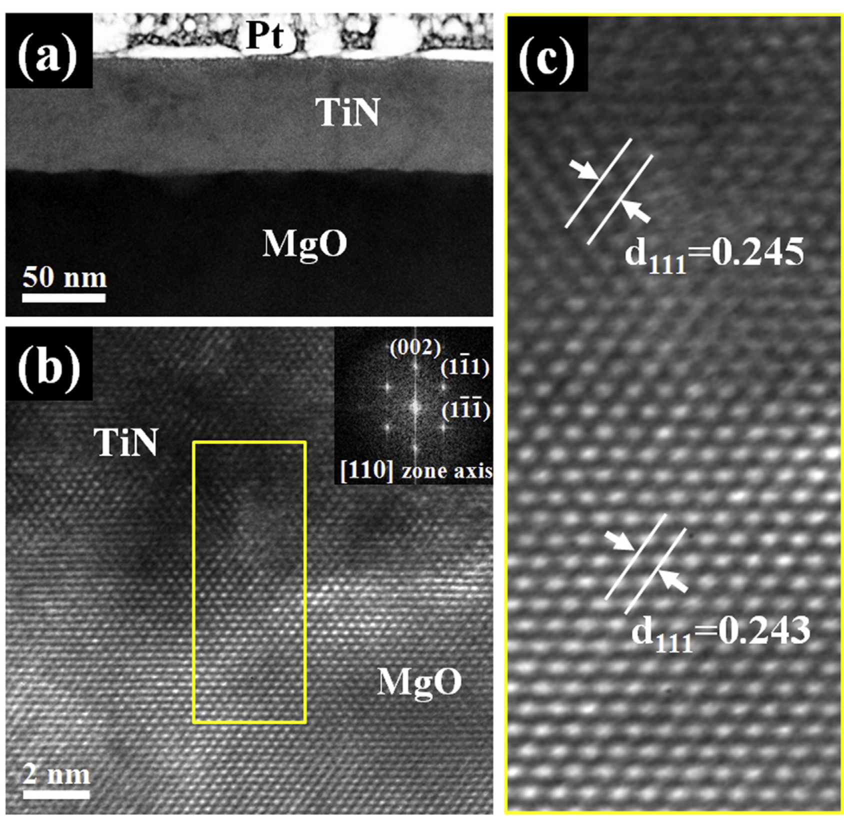

Fig. 1. (a) A low magnification HAADF image of the TiN/MgO interface and (b) Cross-sectional HREM image showing TiN epitaxial with MgO, (c) Enlarged and filtered image of the framed interface region in (b).

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