Formation and Dielectric Properties of Anodic Films Formed on Ta-W Alloys at Various Formation Voltages

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ABSTRACT

Barrier-type anodic films are formed on magnetron sputtered Ta-W alloy films to various formation potentials in 0.1 mol dm⁻³ ammonium pentaborate electrolyte. The anodic films consist of two layers, comprising an outer thin Ta₂O₅ layer free from tungsten species and an inner layer containing both tantalum and tungsten species. Slower migration of W⁶⁺ ions with respect to Ta⁵⁺ ions results in the formation of the two-layered films. Because of the absence of more soluble tungsten species in the outer layer, the anodic films grow at high current efficiency. The reciprocal of capacitance of the anodic films changes linearly with formation voltage, as a consequence of linear thickening of the anodic films with the formation potential. The capacitance is enhanced by the addition of tungsten, particularly at low formation potential. The shift of the potential, at which the anodic film growth commences, to the noble direction, contributes to the enhanced capacitance at the low formation voltages.

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1. Introduction

Anodizing of tantalum has been studied extensively because of fundamental interest in ionic transport in amorphous oxides^{1–9} as well as practical importance as dielectrics.^{10–16} The exceptionally high chemical stability of anodic oxide films on tantalum ensures their growth at nearly 100% current efficiency in a wide range of electrolytes and pH. The anodic oxide films are usually composed of an amorphous material and the growth of the amorphous anodic films proceeds both at the metal/film and film/electrolyte interfaces by migration of anions inwards and of cations outwards, respectively, in a cooperative manner.¹⁷ The transport number of cations in growing anodic Ta₂O₅ was reported to be ~0.24,³ but it was also dependent upon the electrolyte temperature and current density.⁹

The anodic films are usually contaminated with the species derived from electrolyte anions. Their distribution is dependent on the mobility of the incorporated species in the growing anodic films. For instance, the incorporated phosphorus species from phosphoric acid migrates inwards, distributing in an approximately outer half of the anodic films on tantalum. Silicon species are immobile, while the boron species migrates outwards.⁵ Thus, the films are usually two layers, comprising an outer layer contaminated with electrolyte-derived species and an inner layer of relatively pure Ta₂O₅. Fluoride species, migrating inwards, has faster migration rate in comparison with O²⁻ ions, leading to the development of a fluoride enriched region of TaF₅ between the tantalum substrate and the anodic film.⁶

Since the tantalum oxide is an important dielectric in electrolytic capacitors and metal/insulator/metal capacitors, the dielectric properties of anodic tantalum oxide have also been examined.^{10–16} Due to strong demand of down-sizing of tantalum capacitors, further capacitance enhancement and reduction of sintered tantalum powders are requested in capacitor industry. Incorporation of foreign species into the anodic tantalum oxide films is one of the promising ways to enhance the capacitance. The foreign species can be incorporated from substrate as well as electrolyte. The concentration

of the electrolyte-derived species is usually less than 5 at%, such that the control of the dielectric properties by incorporation of electrolyte-derived species is limited. The anodic films formed on alloys have been investigated to examine the growth mechanism and dielectric properties.^{10,18–26} In this study, we have examined the formation and dielectric properties of anodic films formed on Ta-W alloys. Tungsten has been selected since the permittivity of WO₃ ($\epsilon_{\text{ox}} = 42$) is higher than that of Ta₂O₅ ($\epsilon_{\text{ox}} = 27$). To examine the influence of formation potential on the dielectric properties, the anodic films have been formed at a range of formation potentials between 5 and 80 V vs. Ag/AgCl. Capacitance enhancement by the addition of tungsten, particularly at low formation potentials, has been found in this study.

2. Experimental

Tantalum and Ta-(13, 26, and 52 at%) W alloy films, approximately 200 nm thick, were prepared by DC magnetron sputtering on to flat glass substrate as well as 99.99% pure aluminum substrate, which was electropolished and subsequently anodized to 200 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte to provide flat surface. The targets used for the preparation of the alloy films were 99.9% tantalum disk with appropriate numbers of 99.999% tungsten plates located symmetrically on the erosion region. The tantalum disk without tungsten was used for the preparation of the tantalum films. The tungsten content in the alloy was determined using a JEOL JXA-8900M electron microprobe. The specimens were anodized to selected formation potentials up to 80 V in stirred 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K, using a three-electrode cell with a platinum counter electrode and a Ag/AgCl reference electrode. A constant current density of 50 A m⁻² was applied before reaching the selected formation potential. Electrochemical impedance measurements were carried out in the same electrolyte by applying 50 mV(rms) of sinusoidal alternating voltage in the 10⁰ to 10⁴ Hz range, and the capacitances of the anodic oxide films were determined by analyzing the Bode

Figure 1. (Color online) X-ray diffraction patterns of the magnetron-sputtered tantalum and Ta-W alloy films containing 13, 26, and 52 at% tungsten.

diagrams. Vertical cross-sections of the anodic oxide films were observed using a JEOL JEM-2000FX transmission electron microscope (TEM) operating at 200 kV. Electron transparent sections, about 20 nm thick, were generated using a Reichert-Nissei Ultracut S ultramicrotome with a diamond knife. The structures of the deposited tantalum and Ta-W alloy films were identified by grazing incidence X-ray diffraction (GIXRD) using Cu K α radiation with the incident angle of 2°. Compositions of anodic films and alloy films were determined by EPMA. Further, depth profiling analyses of the anodic films were undertaken by glow discharge optical emission spectroscopy (GDOES) using a Jobin-Yvon 5000 RF instrument in an argon atmosphere of 850 Pa by applying RF of 13.56 MHz and power of 35 W. Light emissions of characteristic wavelengths were monitored throughout the analysis with a sampling time of 0.01 s to obtain depth profiles.

3. Results

3.1 Phases of the Ta-W alloy films

Figure 1 shows XRD patterns of the sputter-deposited tantalum and Ta-W alloy films. The tantalum film has a tetragonal structure, which is the high-temperature stable β phase. The formation of the β -Ta phase has often occurred during the deposition by magnetron sputtering.²⁷ The β phase is also found in the Ta-13 at% W film, but it transforms to the bcc phase after adding 26 at% or more tungsten. Since the Ta-W alloy system forms complete solid solutions at equilibrium, all the alloy films deposited in this study appear to be single phase solid solutions.

3.2 Characterization of the anodic films

The deposited films were anodized galvanostatically at 50 A m⁻² in 0.1 mol dm⁻³ ammonium pentaborate electrolyte. As shown in Fig. 2 the formation potential increases almost linearly with time after an initial voltage surge of ~3 V, which is associated with the presence of an air-formed film on the deposited metallic material. The slope increases gradually with the alloy tungsten content from 1.85 V s⁻¹ for tantalum to 2.04 V s⁻¹ for the Ta-52 at% W. The higher slopes for the alloy film in comparison with that of tantalum suggests the growth of the anodic films on the alloys at high current efficiency.

Figure 2. (Color online) Potential-time responses of the sputter-deposited tantalum and Ta-W alloy films containing 13, 26, and 52 at% tungsten during anodizing at 50 A m⁻² to 80 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 298 K.

Transmission electron micrographs of ultramicrotomed sections of the tantalum and Ta-W alloy films anodized to 80 V reveal the formation of barrier-type amorphous anodic films of uniform thickness (Fig. 3). Slightly uneven appearance of the film/electrolyte interface on the Ta-52 at% W is associated with the difficulty of sectioning of the specimen by ultramicrotomy because of increased hardness of the alloy. The amorphous nature of the anodic films is evident from the absence of diffraction contrast. Selected area diffraction patterns of the anodic films revealed only diffuse rings, also confirming the amorphous nature of the anodic films. The thicknesses of the anodic films are 134, 131, and 128 nm for the Ta, Ta-26 at% W, and Ta-52 at% W, respectively, decreasing slightly with an increase in tungsten content. The formation ratio of the tantalum film, calculated from the film thickness formed to 80 V, is 1.7 nm V⁻¹, being close to the previously reported value.²⁸ Similar value of 1.69 nm V⁻¹ was also reported for the anodic film formed on tungsten in 14.7 mol dm⁻³ phosphoric acid,²⁹ such that only a slight change in film thickness with alloy composition is found in this study. The anodic films formed to a low formation potential of 5 V are also reduced by the addition of tungsten from 19 nm for tantalum to 15 nm for the Ta-52 at% W (Fig. 4). The thickness reduction by the tungsten addition is 0.79 at 5 V, which is smaller than that at 80 V (0.96) for the Ta-52 at% W. From the thickness of the anodic films at 5 V, the formation ratio at the low formation voltages appears to be larger than that at high voltages. It has been reported that the more hydrated films are formed at low formation voltages. The voltage-dependent hydration degree of the anodic films may be one of the reasons for the change in the formation ratio at the low formation voltage.³⁰

GDOES depth profiles of the anodic films formed on the Ta-W alloys (Fig. 5) disclose that the films consist of two layers; an outer thin layer is composed of tungsten-free Ta₂O₅ and an inner layer contains both tantalum and tungsten species. The boron species, incorporated from the electrolyte, distributes mainly in the outer Ta₂O₅ layer. The wavy profiles of tantalum and tungsten in the anodic films are artifact, due to interference of lights emitted from the respective elements. The sputtering time to the alloy/film interface becomes shorter with an increase in tungsten content. The reduction of the sputtering time by the addition of tungsten is larger than that of the film thickness, indicating that the sputtering rate of the anodic films increases with the tungsten content.

3.3 Dielectric properties

Figure 6 shows the Bode diagrams of the sputter-deposited Ta-52 at% W alloy films anodized to several formation potentials.

Figure 3. Transmission electron micrographs of ultramicrotomed sections of the sputter-deposited (a) Ta, (b) Ta-26 at% W, and (c) Ta-52 at% W anodized to 80 V at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K.

Figure 4. Transmission electron micrographs of ultramicrotomed sections of the sputter-deposited (a) Ta, (b) Ta-26 at% W, and (c) Ta-52 at% W anodized to 5 V at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K.

Figure 5. GDOES depth profiles of the anodic films formed on the sputter-deposited (a) Ta, (b) Ta-26 at% W, and (c) Ta-52 at% W to 80 V at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K.

Figure 6. Impedance Bode diagrams of the sputter-deposited Ta-52 at% W specimen anodized at 50 A m^{-2} to several formation potentials in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K. The impedance measurements were conducted in the same electrolyte. The equivalent circuit used for the least square fitting is also shown.

All the specimens show linear impedance change with frequency over a wide frequency range with a slope close to -1 and phase shift of nearly -90° in the frequency range below 100 Hz, which are typical of dielectric materials. The impedance increases with an increase in the formation voltage, being associated with a decrease in the capacitance. The tantalum and other Ta-W alloy specimens anodized to the same voltages also revealed similar impedance spectra. The Bode diagrams were fitted using an equivalent circuit shown in Fig. 6 and the capacitances of the anodic films were determined.

The capacitance, C_p , of the anodic films can be expressed using the following equation,

$$C_p = \epsilon_0 \epsilon_{\text{ox}} S / d \quad (1)$$

in which ϵ_0 is the permittivity of vacuum, ϵ_{ox} the specific permittivity, S the surface area, and d the thickness of the anodic film. Since the thickness of the anodic films change linearly with the formation potential, a linear correlation should be found between the reciprocal of the capacitance and the formation voltage. In fact, Fig. 7 shows the linear change in the reciprocal of the capacitance of the anodic films formed on the tantalum and Ta-W alloy films with the formation potential. Obviously, the capacitance is enhanced by the addition of tungsten at all the formation potentials examined.

Figure 7. Change in the reciprocal of the capacitance of the anodic films with the formation potential. The anodic films were formed on the sputter-deposited Ta and Ta-W alloys containing 13, 26, and 52 at% tungsten at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K.

Figure 8. The capacitance of the anodic films formed on the Ta-W alloys with respect to that on tantalum as a function of the formation potential.

The capacitance of the anodic films formed on the Ta-W alloy films with respect to that on tantalum reveals that the capacitance enhancement by the addition of tungsten is more remarkable at lower formation potentials (Fig. 8).

4. Discussion

4.1 Growth of the anodic films

GDOES depth profiles of the anodic films formed on the Ta-W alloys (Fig. 5) reveal the absence of tungsten species in the outer part of the anodic films. Transmission electron micrographs disclose the amorphous structure of the anodic films (Figs. 3 and 4). Thus, the anodic films should be formed by simultaneous migration of cations outwards and anions inwards. The transport number of cations is 0.24 and 0.37 for anodic Ta_2O_5 and WO_3 respectively.²⁸ Since the transport number of cations in growing amorphous anodic films formed on binary valve metal alloys changes linearly with alloy composition,^{31,32} the transport number of cations in the anodic films formed on the present Ta-W alloys should be between 0.24 and 0.37. Assuming the same sputtering rate of the outer and inner layers of the anodic films during GDOES depth profile analysis, the thickness of the outer tungsten-free layer with respect to the total film thickness is estimated to be 0.20 or less, suggesting that the tungsten species are present in the film region above the marker plane as illustrated in Fig. 9. Boron species, incorporated from the

Figure 9. (Color online) Schematic illustration showing the growth of the anodic films on a single-phase Ta-W alloy.

Figure 10. (Color online) The capacitance of the anodic films formed to 80 V on the sputter-deposited tantalum and Ta-W alloy films at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K as a function of tungsten content in alloy.

electrolyte, distribute in the outer layer free from tungsten species. In anodic Ta_2O_5 films, boron species migrate outwards.⁵ Thus, the distribution of the boron species to the depth of the boundary between the outer and inner layers also indicates the outer migration of tungsten species in the present anodic films. Under this situation, both tantalum and tungsten species migrate outwards, with the latter migrating slower than the former species. As a consequence, the faster migrating tantalum species form the thin outer layer free from tungsten species. This means that only tantalum oxide contacts with the electrolyte at the film/electrolyte interface. This should be the main reason of the efficient film growth on the Ta-W alloys, although tungsten does not form the anodic films at high current efficiency in neutral electrolytes. High chemical stability of the anodic films in various corrosive environments is also expected due to the presence of the outer Ta_2O_5 layer free from tungsten species.

4.2 Dielectric properties

As described above, the formation ratios of the anodic films formed on tantalum and tungsten are similar and the permittivity of anodic WO_3 ($\epsilon_{\text{ox}} = 42$) is larger than that of anodic Ta_2O_5 ($\epsilon_{\text{ox}} = 27$). Since the capacitance of the amorphous anodic films on the valve metal binary alloys is usually a compositional average of those on the individual constituting metals,³¹ the addition of tungsten to tantalum should increase the capacitance of the anodic Ta_2O_5 . As expected, Fig. 10 reveals the linear increase in the

Table 1. Change in the V_0 values with alloy composition, estimated from the linear correlation between C_p^{-1} and the formation voltage for the anodic films on the sputter-deposited Ta and Ta-W alloy films.

Composition	V_0/V vs. Ag/AgCl
Ta	−0.99
Ta-13 at% W	−0.17
Ta-26 at% W	−0.045
Ta-52 at% W	0.20

capacitance of the anodic films formed on the Ta-W alloys with alloy tungsten content. The capacitance of the anodic film formed to 80 V on the Ta-52 at% W is 1.2 times that on the tantalum.

More interesting results are obtained at low formation potentials. As shown in Fig. 8 the capacitance enhancement by the addition of tungsten is more significant at lower formation potentials and the capacitance of the anodic film on the Ta-52 at% W at 5 V is as high as 1.43 that on tantalum at the same formation potential. Since the reciprocal capacitance of the anodic films on the Ta-W alloys changes linearly with the formation potential, the permittivity of the anodic films may not be potential dependent. The most probable explanation of the higher capacitance enhancement at the low formation potentials is the change in the potential that the anodic films growth commences. When the anodic film growth commences at the potential of V_0 , the capacitance of the anodic film at the formation voltage of V is expressed as follows,

$$C_p = \frac{\varepsilon_0 \varepsilon_{ox} S}{k(V - V_0)} \quad (2)$$

in which k is the formation ratio. When the V_0 shifts to noble potential by the addition of tungsten, the capacitance, C_p , is enhanced, particularly at low formation potentials. The V_0 values are estimated by fitting the experimental data shown in Fig. 7 using the Eq. (2) and the values are listed in Table 1. It is obvious that the V_0 values ennoble with the content of tungsten. Thus, the ennoblement of the V_0 results in the fact that the capacitance enhancement by the addition of tungsten becomes higher at low formation potentials.

The ennoblement of the V_0 by the addition of tungsten is qualitatively explained by the noble equilibrium potential of W/ WO_3 in comparison with that of Ta/ Ta_2O_5 . However, the equilibrium potential of W/ WO_3 in the ammonium pentaborate electrolyte (pH 8) is −0.35 V vs. Ag/AgCl, which is considerably lower than the V_0 for the Ta-52 at% W. Although the quantitative and scientific understanding of the V_0 values is the subject of future study, the present study demonstrates that the addition of a noble element to the substrate metal is an effective way to enhance the capacitance of the anodic films at low formation potentials. The capacitance enhancement at low formation potentials are of practical importance for recent capacitor applications. Our recent study also revealed that the addition of molybdenum to tantalum also enhanced the capacitance of the anodic films at low formation potentials. The results will be reported separately.

5. Conclusions

Barrier-type, two-layered amorphous anodic films, comprising an outer thin tungsten-free Ta_2O_5 layer and an inner oxide layer

containing both Ta^{5+} and W^{6+} ions, are formed at high current efficiency by anodizing of sputter-deposited Ta-W alloy films with different tungsten contents in 0.1 mol dm^{−3} ammonium pentaborate electrolyte. The addition of tungsten reduces slightly the film thickness and increases the permittivity of the anodic films. The capacitance is, therefore, enhanced by the addition of tungsten. The capacitance enhancement becomes more remarkable at lower formation potentials. This can be explained by the ennoblement of the potential, V_0 , of the commencement of film growth, which is estimated from the linear correlation between the reciprocal capacitance and the film formation potential. The present study demonstrates a promising way of capacitance enhancement of the anodic films by the addition of noble elements from the substrate.

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