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Corrosion behavior of hafnium in anhydrous isopropanol and acetonitrile solutions containing bromide ions

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Abstract: The corrosion behaviors of hafnium in Et_4NBr isopropanol and acetonitrile(ACN) solutions were investigated using electrochemical measurements, ICP-AES and SEM techniques. Results revealed that the open circuit potential gets more positive due to the increased passivity of the surface oxide film with increasing immersion time until it reaches a steady state value. The potentiodynamic anodic polarization curves did not exhibit an active dissolution region near corrosion potential due to the presence of an oxide film on the electrode surface, which was followed by pitting corrosion. SEM images confirmed the existence of pits on the electrode surface. Cyclic voltammetry and galvanostatic measurements allowed the pitting potential (φ_{pit}) and the repassivation potential (φ_p) to be determined. φ_{pit} increased with increasing potential scanning rate but decreased with increasing temperature, Br^- concentration and ACN concentration. The impedance spectra showed that the resistances of the solution and charge transfer decreased with the increase of ACN concentration.

Key words: corrosion behavior; hafnium; acetonitrile; Et_4NBr; electrochemical method; pitting corrosion; passive film

1 Introduction

Ongoing development of the microelectronics, starting from the early 1960s of the 20th century, involves an increase in the integration degree of emerging semiconductor devices, as well as the increase of speed and functionality of integrated circuits (ICs) [1]. But as the semiconductor industry ushered in nanometer era [2], a gate dielectric thickness in the field effect transistor (FET) reached its physical limits because of an increase in leakage currents due to tunneling effects [3]. In order to reduce the leakage current and capacitance of devices, significant attention has been paid to the high-k dielectric layers including HfO_2, Al_2O_3, TiO_2, ZrO and CeO_2 as a substitution of ultra-thin silicon dioxide films [4], among which HfO_2 is considered the most promising [5]. Hafnium alkoxide is mainly used for the deposition of HfO_2 layers by atomic layer deposition (ALD), and deposited in this manner, the hafnium-based high-k dielectrics show much more stable electrical characteristics compared with the ones formed by sputtering or chemical vapors [6].

At present, the most common method of preparing hafnium alkoxides is based on the halide synthesis [7]. This method has multistep processes, and the starting materials are difficult to access. In addition, it involves various by-processes which contaminate the products and decrease their yields [8]. On the other hand, the electrochemical method has great promise for the direct conversion of the less electropositive metals to their alkoxides owing to its simplicity and high productivity as well as its continuous and non-polluting character (with hydrogen as the major by-product). In our earlier works, we prepared several tantalum and niobium alkoxides by electrochemical method [9−11]. In 1995, hafnium isopropanol was obtained for the first time by TUREVSKAYA et al [12] with the electrochemical method involving electrolysis of an isopropanol solution containing tetraethylammonium bromide with a platinum cathode and a hafnium anode. However, the electrochemical behaviors of this process have not been investigated so far.

Hafnium is a valve metal and some literatures have reported its electrochemistry in aqueous solutions [13−18]. BARTELS et al [13] investigated the

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potentiodynamic oxide growth of hafnium in acidic, neutral and alkaline electrolytes and showed that its electrochemistry in acidic electrolytes is characterized by anodic breakdown of the oxides due to localized corrosion. Most investigations were related with the formation of anodic oxide films and the kinetics of dissolution of these films [13,17,18]. Titanium and tantalum, which are close to hafnium in its properties, were investigated in anhydrous alcohols, and the results indicated that they could suffer from severe corrosion [19−22].

Despite some studies on the electrochemistry of Hf in aqueous solutions, only one literature reported the electrochemical behaviors of hafnium in anhydrous ethanol [23]. In the present study, the electrochemical behavior of hafnium was investigated in anhydrous isopropanol and ACN solutions containing supporting electrolytes, by using open circuit potential measurements, cyclic voltammetry, galvanostatic, potentiody-namic anodic polarization, potentiostatic and impedance techniques. ICP-AES method of chemical analysis was also applied to confirming results obtained from electrochemical measurements. SEM examinations of the electrode surface were also performed. The effect of the ACN on the stability of the passive film was discussed.

2 Experimental

Anhydrous isopropanol was supplied by Tianjing Damao Chemical Reagent Corporation, China. Anhydrous acetonitrile (ACN) and Et_4NBr were provided from Sinopharm Chemical Reagent Corporation Limited. The working electrode employed was made from a very pure hafnium rod (99.9%), which was supplied by the Northwest Institute for Non-ferrous Metal Research, China. The electrode used was cut as cylindrical rods and mounted into glass tubes using Araldite to offer an active flat disc shaped surface of 4.28 mm^2 geometric area to contact the test solution. Prior to each experiment, the electrode was successively polished with a series of emery papers from a coarse grade of 1200 to fine grade of 3500. The electrode was then successively rinsed with ethanol and isopropanol and finally dipped in the electrolytic cell.

The experiments were performed in a 250 mL volume glass electrolytic cell utilizing Pt foils of 1 cm × 1 cm and 2 cm × 2 cm as auxiliary and reference electrodes, respectively. All potentials given in this work were referred to this reference electrode. The experiments were carried out in anhydrous isopropanol and ACN (30%−70%) solution containing Et_4NBr of various concentrations (0.02−0.10 mol/L). Each run was carried out in aerated stagnant solutions at the required temperature (±1 °C), using water thermostat. The gases used for studying its effects on the electrode potential of naturally passivated Hf in anhydrous isopropanol and ACN solutions were purified and dried before bubbling in the electrolyte. The gas was bubbled at least 20 min in the test solution prior to electrode immersion. The sample was immersed in the solution until the potential reached a stable value (about 3 h), and then each measurement was performed.

Electrochemical measurements were performed using a potentiostat/galvanostat (CHI660C Electro-chemical Workstation provided by Shanghai CH Instrument Company, China) connected to a personal computer. Cyclic voltammetric measurements were carried out by sweeping the potential linearly from −1 V (vs Pt) more negative than the open circuit potential (φ_{ocp}) up to 3 V (vs Pt) in the positive direction at scanning rate of 5 mV/s, reversing with the same scan rate to the lowest potential, and finally returning to the starting potential to form one complete cycle. The potentiodynamic anodic current/potential curves were recorded from −1.0 V (vs Pt) more negative than the open circuit potential (φ_{ocp}) up to 3 V (vs Pt) with the required scanning rate. In galvanostatic potential/time transients, a constant anodic current density was applied on the Hf electrode and the variation in potential was recorded as a function of time. The potentiostatic measurements were carried out at a given step anodic potential ($\varphi_{s,a}$) at which the current transient was recorded. EIS measurement was carried out using AC signals of amplitude 5 mV in the frequency range from 1 Hz up to 0.1 MHz. All impedance data were fit to appropriate equivalent circuits using computer program ZSimDemo 3.30d.

In order to gain more insight on the composition and the morphology of the passive oxide films grown on the surface of the tested Hf samples, the Hf samples were subjected to a JEOL JSM−6360LV scanning electron microscopy (SEM) analysis. Before performing SEM, the Hf samples were submitted to the same surface treatment, immersed in 0.06 mol/L Et_4NBr isopropanol and ACN (50%) solution after anodic polarization from −1 up to 0.7 V (more negative than the pitting potential) and 2.2 V (more positive than the pitting potential) at 30 °C and a scanning rate of 5 mV/s, and finally preserved in anhydrous ethanol which was deaerated with N_2 for 20 min to remove O_2 dissolved in the solution. The acceleration influence of the applied anodic potential towards pitting corrosion of Hf was evaluated in 0.06 mol/L Br^- solutions at 30 °C, using an independent chemical method of analysis, namely inductively coupled plasma-atomic emission spectrometry (ICP-AES). The Hf^{4+} ions concentration was determined in the aggressive solution as a function

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