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Effect of bromide ions on the corrosion behavior of tantalum in anhydrous ethanol

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ABSTRACT

The electrochemical behaviors of Ta in Et_4NBr ethanol solutions were investigated using potentiodynamic polarization, cyclic voltammetry, potentiostatic current–time transient and impedance techniques. The potentiodynamic anodic polarization curves did not exhibit active dissolution region due to the presence of thin oxide film on the electrode surface, which was followed by pitting corrosion as a result of passivity breakdown by the aggressive attack of Br^- anions. The pitting potential (E_b) decreased with the increase of solution temperature and Br^- concentration, but increased with increasing potential scan rate and water concentration. The incubation time derived from potentiostatic current–time transients decreased with increasing potentials. The impedance spectra exhibited two time constants for all the potentials and the resistance of passive layer decreased with increasing potential.

1. Introduction

In past years, tantalum oxide (Ta_2O_5) has attracted interest in microelectronics as a potential replacement for silicon oxide (SiO_2) as the gate dielectric material for metal-oxide-semiconductor (MOS) technology in very large scale integrated devices (VLSI). In fact, since the decrease in the thickness of the SiO_2 is about to reach its physical limit and at these ultrathin thicknesses the tunnelling currents become too large to maintain a satisfactory device reliability, a solution is to use materials with large dielectric constants to increase the insulator thickness and thus diminish the tunnelling effect. Ta_2O_5, with a relative dielectric constant of about 25 (in its amorphous phase) is of interest because it is compatible with microelectronics manufacturing and forms good quality films under microelectronics compatible processing conditions [1]. Ta_2O_5 films have been deposited by chemical vapor deposition (CVD) using several precursor materials such as $Ta(OC_2H_5)_5$, $Ta(OCH_3)_5$, $TaCl_5$ and $Ta[N(CH_3)_2]_5$. Among theses precursors tantalum ethoxide ($Ta(OC_2H_5)_5$) is often the most preferred one because of its 100% volatility and superior thermal stability [2].

The most common preparation of tantalum alkoxides is based on the tantalum chloride and alcohol [3]. This method has the disadvantage that HCl gas is liberated, as a result of which an apparatus in which the reaction is carried out is subjected to severe corrosion. And the reaction is performed using large amounts of organic solvents which are harmful to the environment. In addition, the necessary reagents are scarce and the reactions involve various side processes which contaminate the products and decrease their yields [4].

For these reasons, the direct electrochemical synthesis of metal alkoxides by anode dissolution of metals in absolute alcohols in the presence of a conductive admixture seems a very promising method. 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) [5]. In 1972 the electrochemical synthesis of tantalum ethoxide by anodic dissolution of tantalum in ethanol in the presence of NH_4Cl as an electroconductive additive was patented [6]. Since then, tantalum ethoxide was prepared by Shreider et al. [7], Turova et al. [8] and our teams [9,10] using the electrochemical method. The electrosynthesis technique has been successfully employed in Russia for the commercial production of alkoxides of Y, Ti, Zr, Nb, Ta, Mo, W, Cu, Ge, Sn, and other metals [5]. Despite the extensive study in the electrochemical synthesis of tantalum ethoxide, to the author's knowledge, little similar literature has been reported on the electrochemical behaviors of this process [11–13]. In the present work, the electrochemical behaviors of tantalum were investigated in anhydrous ethanol containing supporting electrolytes, using potentiodynamic polarization, cyclic voltammetry and current–time transient, which are very useful to understand the reaction mechanism.

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2. Experimental

A tantalum rod (∅2.25 mm × 180 mm) was supplied by Zhuzhou Cemented Carbide Group Corp. Ltd., with a chemical composition (wt.%): O 0.02, C 0.005, N 0.003, Fe 0.005, Ni 0.005, Cr 0.005, Nb 0.002, W 0.002, Mo 0.001, Si 0.002, Mn 0.001, and Ta balance. The apparent exposed area was $0.04\,cm^2$. The electrode was successively polished with a series of emery papers, from a coarse one 400 to fine grade 1200, rinsed with acetone, ethanol, and finally dipped in the electrolytic cell.

The experiments were performed in a 300 ml volume Pyrex glass cell using Pt foil and a saturated calomel electrode (SCE) as auxiliary and reference electrodes, respectively. To avoid contamination, the SCE was connected via a bridge filled with the solution under test, the tip of which was pressed against the surface of the working electrode to minimize the IR drop. All potential given in this paper are referred to this reference electrode. All chemicals used were of analytically pure grade. The electrolyte solutions were prepared from anhydrous ethanol and tetraethylammonium bromide (Et_4NBr). In order to remove the water form AR ethanol, 5–8 g Mg was added into 1 L ethanol. Refluxed for 4–6 h, the anhydrous ethanol was distilled out from the mixture. The operation of pouring the anhydrous into the cell was performed in the Workstation Mbraun Unilab. Prior to the experiments, the solutions were deaerated with N_2 and the electrode was held at −1 V for 300 s to electro-reduce any possible oxidized surface species.

Electrochemical measurements were performed using a potentiostat/galvanostat (CHI 660C Electrochemical Workstation provided by Shanghai CH Instrument Company, China) and connected with a person computer. The potentiodynamic polarization curves were recorded by changing the electrode potential automatically from −1 to 4.0 V at the desired scan rate. Cyclic voltammetric measurements were carried out by sweeping linearly the potential from the open circuit potential into the positive direction at a given scan rate up to the required potential value and then reversing with the same scan rate to the lowest potential, and finally returning to the starting potential to form one complete cycle. The anodic current transients at a constant anodic potential E_a were recorded for 300 s. Each experiment was performed with freshly prepared solution and a newly polished set of electrodes. All measurements were carried out at room temperature (25 ± 1 °C).

3. Results and discussion

Fig. 1 shows potentiodynamic polarization curve recorded for Ta in anhydrous ethanol containing 0.1 M Et_4NBr with a scan rate of 10 mV/s. On the positive going scan, the cathodic current density decreases gradually forming a small cathodic current plateau just before reaching a zero value at the corrosion potential (E_{corr}). This plateau probably corresponds to hydrogen evolution reaction on the tantalum surface. The anodic excursion span does not exhibit active dissolution region near E_{corr}. The lack of active dissolution can be attributed to spontaneous passivation of Ta due to presence of oxide film on the electrode surface. In fact, tantalum itself is an active metal from an electrochemical point of view since its domain of thermodynamic stability is found to lie below that of water reduction at all temperatures from 25 to 300 °C [14]. With the increase of the anodic potential, the passive current density increases gradually, which may correspond to the replacement of chemically dissolved oxide film by Br^- anions.

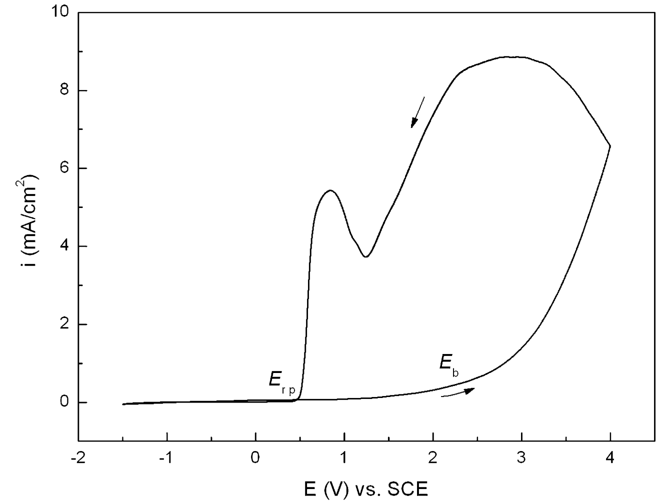

Fig. 1. A typical cyclic voltammogram of Ta in anhydrous ethanol containing 0.1 M Et_4NBr with a scan rate of 10 mV/s.

However, when the anodic potential exceeds a certain critical value E_b, the current density rises suddenly, without any sign of oxygen evolution, suggesting breakdown of the passive film, initiation and propagation of pitting corrosion. The current density continues even after the potential sweep reversal, autocatalytic character of pitting [15]. Afterwards, the current density begins to decay linearly and then an anodic peak is observed during polarization in the negative direction, which may be attributed to the oxidization of the intermediates produced and absorbed on the tantalum surface [16]. As a result, a hysteresis loop is formed, a characteristic of pitting corrosion phenomenon [17]. This hysteresis loop allows the repassivation potential E_{rp} to be determined, where E_{rp} corresponds to the potential values below which no pitting occurred and above which pit nucleation begins [18].

According to Hoar's theory, the breakdown of the passive film and the initiation of pitting attack can be ascribed to the adsorption of Br^- ions on the passive film. The adsorbed aggressive anions can penetrate through passive layer especially at its defect points and flaws with the assistance of a high electric field to reach the base metal surface. Following this, pit growth occurs as a result of increasing the concentration of Br^- resulted from its migration [19,20].

Fig. 2 illustrates the solution temperature effect on the cyclic voltammograms of Ta in 0.1 M Et_4NBr solution of anhydrous ethanol. The rise of temperature enhances the heights of the anodic peaks. At the same time, the curves shift to the negative direction corresponding to an increased susceptibility to pitting, which imply that increasing solution temperature is destructive to the

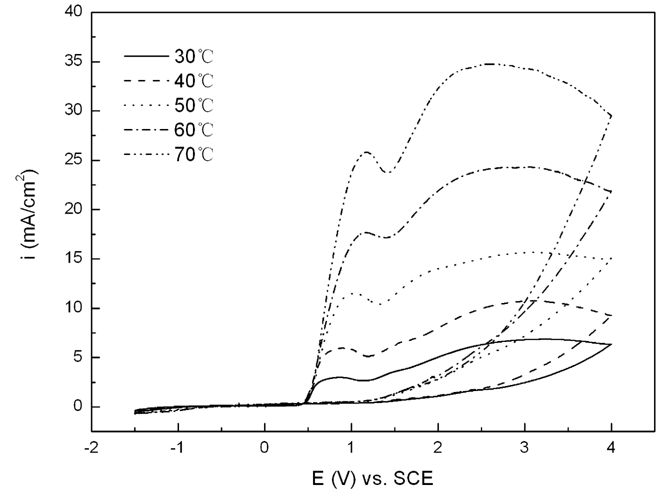

Fig. 2. Effect of temperature on the cyclic voltammograms of Ta in anhydrous ethanol containing 0.1 M Et_4NBr.