Effects of Thermal Oxide of Ta on Anodic Oxide of Ta

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Abstract

The paper is dedicated to thermal oxide film of Ta, which forms on the surface of Ta anodes when they are exposed to air after sintering (passivation process) and subsequently incorporates into anodic oxide film of Ta during anodizing process. The passivation with rapid and controlled air pressure increase was investigated on anodes with different CV/g powders, and its effect on the structure of anodic oxide films was demonstrated.

Introduction

Thermal oxide film (TOF) forms rapidly on the surface of Ta anodes when they are exposed to air after sintering in vacuum (passivation process). During subsequent anodizing, the TOF incorporates into growing anodic oxide film (AOF) of Ta, which is employed as the dielectric in Ta capacitors. When formed at room temperature, the TOF is about 3 nm thick, which is much less than the thickness of the AOF (typically 20 nm - 800 nm, depending on formation voltage). Incorporation of very thin natural surface oxide into much thicker AOF practically does not affect the structure and dielectric properties of the AOF, and, thereby, the performance and reliability of Ta capacitors. This situation is typical for anodes with low CV Ta powder, having low surface-to-volume ratio in coarse powder particles. In these anodes, the TOF grows thicker only if they are exposed to air at elevated temperatures before they cool down to room temperature after sintering.[1]

The situation can be different at passivation of high CV powder with large surface-to-volume ratio in fine powder particles. This powder generates more heat during passivation due to exothermic nature of Ta-O chemical reaction, while its ability to dissipate heat is less than that in coarse powder. When heat release offsets heat dissipation, anode temperature starts to rise. The temperature increase stimulates further TOF growth, which generates more heat and causes further temperature increase. Eventually, the temperature can reach igniting point at which the anodes begin to burn. An increase of oxygen content in the bulk of Ta anode intensifies thermal oxidation and decreases the igniting temperature.[2-3]

When TOF becomes thicker, its growth rate is controlled by oxygen diffusion through the oxide film from air to the Ta surface. Increasing of the TOF thickness and, thereby, diffusion length, slows down oxidation process. As a result, the anodes can start cooling down after reaching maximum temperature (Tmax), where heat dissipation offsets heat release. The final TOF thickness depends on Tmax and the total time that the anodes were exposed to elevated temperatures and can exceed significantly the thickness of the natural surface oxide. The thicker TOF is not uniform and amorphous, as is the natural surface oxide. It is characterized by dendrite-like morphology, non-uniform chemical composition, and presence of crystalline inclusions in the amorphous matrix of the film.[4] Incorporation of the thicker TOF into the AOF can change structure and dielectric properties of the AOF and thereby affect the performance and reliability of Ta capacitors.[4-5]

Data presented in the literature on the structure and properties of TOF were obtained on Ta foils with different TOF thickness, which was controlled by annealing of the foil in air. This paper investigates porous anodes sintered in vacuum with 50k CV/g and 150k CV/g Ta powders. The anodes were cooled down in an inert atmosphere to room temperature after sintering. Passivation was performed by anode rapid exposure to air (rapid passivation) and by gradual increase of air pressure in the passivation chamber (controlled passivation). The anode temperature and air pressure were monitored during passivation. High

resolution scanning electron microscopy (HRSEM), Leco oxygen analysis, and wet electrical test were used to characterize TOF and AOF on Ta anodes.

Results and Discussion

Fig. 1 demonstrates temperature profiles at passivation of anodes with 50k CV/g powder. The temperature monitoring was performed by thermocouple (TC) firmly attached to anodes inside the crucible, TC outside the crucible, and pyrometer focused on the crucible wall.
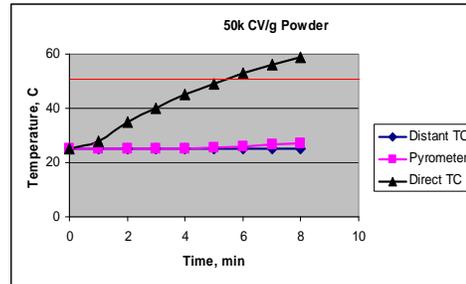

Fig. 1. Temperature control at passivation

As one can see, only the TC inside the crucible shows rapid increase of anode temperature during passivation, while the distant TC and pyrometer show very little temperature change. Obviously, relatively low thermal conductivity of porous anodes and heat dissipation in the crucible make the distant TC and pyrometer inefficient for monitoring the actual anode temperature at passivation. Consequently, the TC inside the crucible with anodes was used for the experiments on passivation.

Fig. 2 demonstrates temperature profiles at rapid and controlled passivation of anodes sintered with 50k CV/g powder.
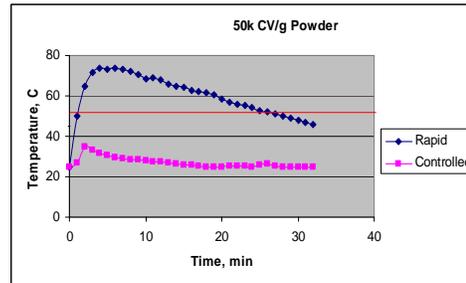

Fig. 2. Temperature profiles at passivation 50k CV/g anodes.

The Tmax and total time anodes were exposed to elevated temperatures were much higher at rapid passivation than these at controlled passivation. This indicates a larger amount of TOF formed on Ta anodes with rapid passivation. However, average oxygen readings were almost identical in anodes with rapid and controlled passivation. The average Cap, DF and DCL readings at wet electrical test with 30V – 80V formation voltages were also comparable for rapid and controlled passivation.

Fig. 3 shows typical images of the surface of Ta anodes sintered with 50k CV/g powder with rapid and controlled passivation and formed to 80V.
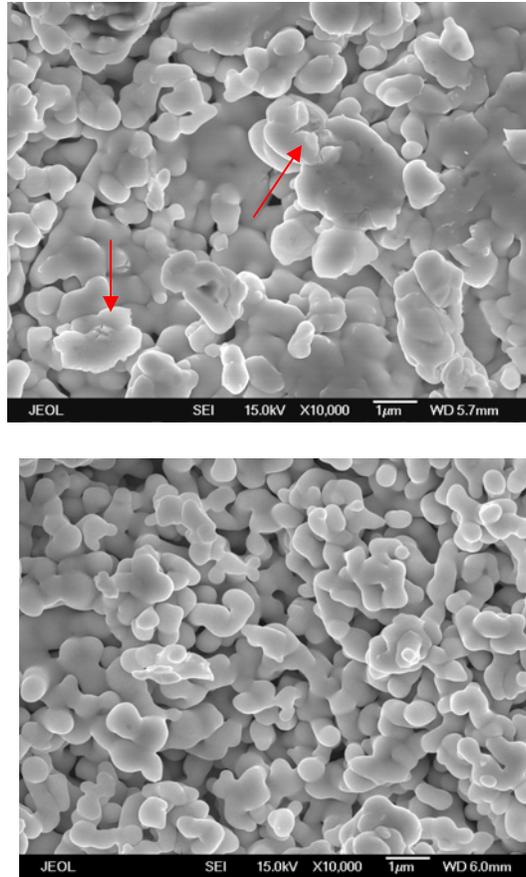
Fig. 3. Surface of 50k CV/g anodes with rapid (top) and controlled (b) passivation

The AOF on anodes with rapid passivation has numerous areas of small cracks. The pattern of these defects is typical for crystal growth in the amorphous matrix of the AOF. The density and size of the defects vary for different areas on anode surface and also differ for different anodes in the crucible. At the same time, the AOF on the surface of anodes with controlled passivation is typically free of cracks and disruptions. No cracks or other defects were detected in the core of anodes with either rapid or controlled passivation (Fig. 4).
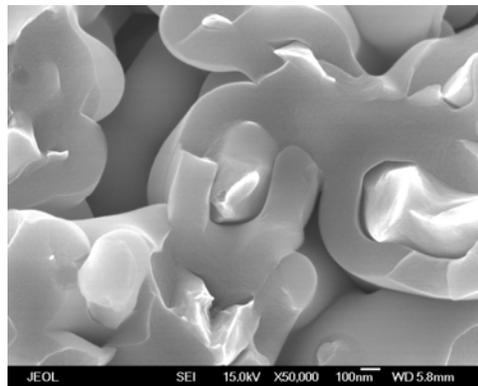

Fig. 4. Core of 50k CV/g anode with 80V formation voltage

According to Fig. 3 and Fig. 4, rapid passivation forces crystallization of the AOF in some local areas on the anode surface, while no crystals were detected on the surface of anodes with controlled passivation or

in the anode core with either rapid or controlled passivation. From that, crystallization of the AOF can be attributed to thick TOF in some areas on the surface of anodes with rapid passivation. When incorporated into the AOF, thick TOF stimulates field crystallization due to crystalline inclusions in the amorphous matrix of thermal oxide.

The local areas with thicker TOF, formed at rapid passivation, are relatively small versus total anode surface. That is why the average oxygen readings are similar for both rapid and controlled passivation. The wet electrical test results are not sensitive to small cracks in AOF caused by crystal growth, while crystals are hidden inside the amorphous matrix. At the same time, the crystals continue to grow during high temperature manufacturing steps, testing, and field application and eventually cause the AOF disruption and sharp DCL increase in Ta capacitors.

Uneven TOF growth at passivation was also detected on anodes with 150k CV/g powder. In this case, the anodes were rapidly exposed to air for a short time (1 min) to prevent burning (Fig. 5).
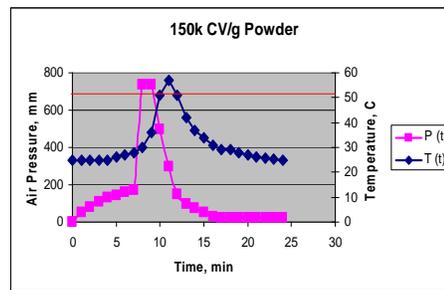

Fig. 5. Air pressure and temperature profiles at rapid passivation of 150k CV/g anodes

As one can see, the temperature increase during this short exposure to air was relatively small, below igniting temperature for the 150k CV/g powder. Similarly to 50k CV/g powder, controlled passivation of anodes with 150k CV/g powder was performed by gradual increase of air pressure in the passivation chamber to keep the anode temperature below 50 ^{o}C. Analysis of the oxygen content in sintered anodes and wet electrical test at 12V formation voltage showed practically identical results for rapid and controlled passivation.

Fig. 6 demonstrates burned spots on the surface of 150k CV/g anodes sintered with rapid passivation.
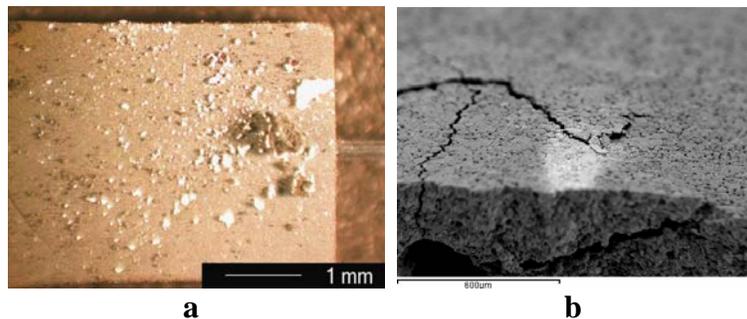

a   b

Fig. 6. Burned spots on 150k CV/g anodes

The burned spots relate to excess powder on the anode surface (Fig. 6a) but also can be seen on a clean anode surface (Fig. 6b). Fig. 7 shows a magnified image of the burned spot in Fig. 6b.
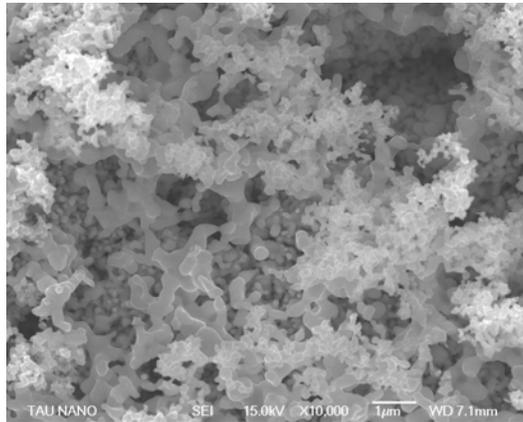
Fig. 7. Burned spot on 150k CV/g anode

As one can see, the burning occurred in an area with finer prime particles than the prime particles in surrounding area of the anode.   No burned spots were detected on the surface of anodes with controlled passivation and in the core of anodes with either rapid or controlled passivation.

Fig. 8 demonstrates the local area in the vicinity of the burned spot on the surface of 150k CV/g anode anodized to 12V.
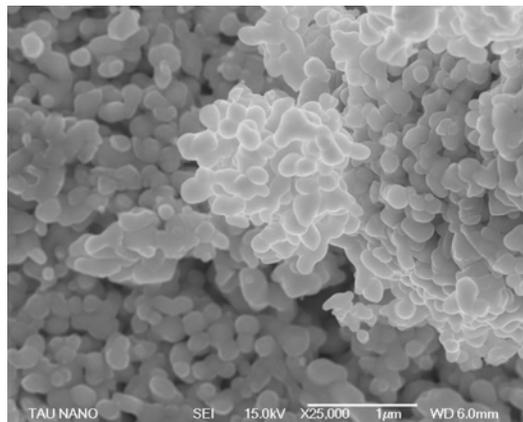

Fig. 8. Area near to the burned spot on the surface of 150k CV/g anode

Rapid TOF growth, forced by high temperature at burning, can be the reason for clogging pores between prime particles in this area. As a result, the TOF thickness exceeds the thickness of the AOF in local area on anode surface.

Conclusion

Results presented in this paper show that there are local areas on the anode surface where thermal oxide can grow at an accelerated rate when anodes are exposed to air after sintering. These areas can be attributed to agglomerates of fine particles, excess powder on the anode surface, anode corners, etc. They are also more prevalent in the top layer of anodes in the crucible. In all these cases, the balance between heat generation and heat dissipation is shifted toward heat generation.

After anodizing, areas of an anodic oxide with thick thermal oxide on the anode surface are more prone to crystallization than the areas with thin natural thermal oxide. This is due to crystalline inclusions in the bulk of the thermal oxide. The density and size of these inclusions increase with increasing thickness of the thermal oxide. This situation is more dangerous for high voltage Ta capacitors where crystallization of the anodic oxide film is the major reason for degradation and catastrophic failures.

In low voltage, high CV tantalum capacitors, local thickness of the thermal oxide can exceed the thickness of anodic oxide formed at low formation voltage. Having TOF instead of AOF as the dielectric in some areas on the surface of Ta anode, can cause DCL increase and instability, since dielectric properties of TOF are inferior to dielectric properties of AOF.

To avoid negative impact of thermal oxide on the anodic oxide of tantalum, the temperature at passivation should stay close to room temperature. This can be accomplished within a limited amount of time via controlled air pressure increase and efficient heat exchange in the passivation chamber. Specific conditions of controlled passivation depend on powder CV, anode size, crucible load, and total weight of sintered anodes.

Acknowledgment

Literature

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NOTE:
This paper was recognized as "2006 Outstanding Paper" determined by votes from attendees at this conference. The award was presented at the 2007 CARTS-Europe conference in Barcelona, Spain, in September, 2007.