Overcoat Failure Mechanisms In Thermal Ink Jet Devices

L. S. Chang, J. O. Moore and J. M. Eldridge
Research Division, IBM Corp. San Jose, California

Introduction

Passivation layers on thermal ink jet devices are subjected to exceedingly severe stress conditions. Thermal fatigue, chemical and electrochemical processes and cavitation-erosion can interact synergistically to disrupt the passivation, causing heater burnouts. Some earlier printheads used a double dielectric layer of a-Si_xC_{1-x}:H on a-Si_xN_{1-x}:H as overcoats[1] but Ta is now widely employed as the top passivant layer. In the absence of artifacts, thermal oxidation of the carbide and tantalum will be seen to basically limit printhead lifetimes. Addition of a noble metal to the Ta surface retards this oxidation and can yield devices having outstanding lifetimes. This paper discusses in phenomena in general and attempts to clarify certain fundamental overcoat wearout processes.

Experimental Results and Discussion

Heaters are most easily tested by immersion in an open-pool aqueous solution but functional devices are covered, operating under closed-pool conditions. One can effectively go from open- to closed-pool life test conditions by introducing a second wall above the heater and vary the separation[2]. Decreasing the separation increases lifetimes for heaters passivated with a Plasma Enhanced Chemically Vapor Deposited (PECVD) overcoat of Si_xC_{1-x}:H, tested in a glycol-water solution (see Figure 1). Extrapolating the data to a ≈ 25 microns shows that open-pool testing reduces lifetimes by about 30X, relative to that in actual jetting devices. Correspondingly, Scanning Electron Microscopy (SEM) shows the overcoat failure mechanism generally changes from a cavitational to a non-pitting process, typical of a generalized chemical attack. The presence of a second wall acts to reduce the bubble collapse velocity and mitigate cavitation.

pH effects on overcoat life provides another reason to discount cavitation (see Figure 2). The removal rate of Si_xC_{1-x}:H increases with pH[2] and is due to the conversion or carbide at its outer surface to SiO_2. Extensive X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) measurements show the PECVD carbide surface is comprised of SiO_2 whose thickness depends upon ambient exposure and composition.[3-5] Bulk SiC itself is not soluble in aqueous acids or bases but bulk SiO_2 is slightly, becoming more so at higher pH's.[6] The rate of silica dissolution is increased significantly by vigorous stirring. Therefore Si_xC_{1-x}:H thinning during device operation resembles the dissolution of SiO_2. Cavitation is not important other than providing a strong stirring action. Since the carbide composition can be varied, one might note that our oxidation results suggest that the carbide composition be kept at x ≈ 0.5 to reduce the rate.[5] Films of this composition are also harder and thus more cavitation-resistant.[7]

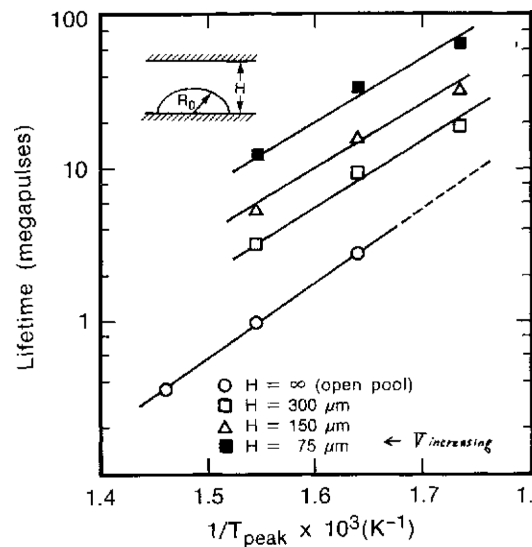

Figure 1. Effects of spacing of a parallel plate from the heater plane on lifetime.

Printheads with sputtered Ta top overcoats exhibit excellent reliability, typically lasting a billion firing cycles or more. Kogative effects can offset this and can result from poor ink chemistry and overdriven heaters. Tantalum film stress, thickness and adhesion must also be controlled to prevent delamination and cracking.

Ta overcoats, like PECVD carbide overcoats, fail largely because of cavitation during *open-pool testing.*[8] The cavitation ejects small grains of metal, especially

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where bubble collapse forces are largest. AES and SEM findings indicate two more or less distinct types of attack: embrittlement of regions exposed to maximum bubble collapse pressures; and, localized pitting. The embrittled areas are relatively oxygen-rich. Apparently, Ta failures under open-pool testing involves a strong chemical contribution as well.

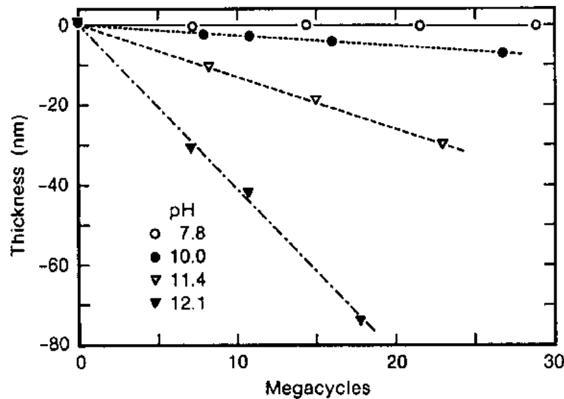

Figure 2. pH effects on etching Si_xC_{1-x}:H overcoats during bubble generation and collapse.

Such phenomena must depend on the Ta- O metallurgical system. The Ta- O phase diagram indicates the solubility of oxygen in bulk, solid tantalum is under 0.5 at % near room temperature[9] but films often contain a few at % O or more, depending on processing. Oxygen in excess of the solubility limit precipitates as oxides at grain boundaries to harden the material but some oxygen may be held in solution. Yoshirara and Suzuki[10] have shown that room ambient exposures markedly increases compressive film stresses in Ta, due to oxygen pickup via grain boundaries. The rates depend on microstructure which is controlled by the sputtering process. Temperatures of even 100C accelerate oxygen diffusion and rates of stress increases. Such changes will be greater in ink jet devices.

While the oxidation behavior of the bulk α-phase of Ta is well known, understanding of the oxidation of α- and β- Ta films is limited. We carried out one study using thermally-pulsed heating to approximate the ambient of the device.[11] Sputtered Ta films were deposited on thin film heaters to prepare test structures. The Ta films were highly textured, consisting almost entirely of the metastable, body centered tetragonal β-phase with at most 5 vol.% body centered cubic α- phase. (While little has been published on Ta phase and morphology effects on ink jet reliability, it may be relevant to remark that β-Ta films are more stable when employed in thin film capacitors[13]). The Ta/heater structures were thermally-pulsed in air under various relative humidities, using typically 5 microsec/pulse at a frequency of 2 kHz and total cycle times up to 600 megacycles. Peak oxidation temperatures were estimated from a 2-dimensional thermal model.[12]

AES measurements show oxidation causes the growth of a Ta_2O_5 surface oxide and substantial oxygen penetration into the interior, as expected from the literature. Profilometry measurements readily detect height increases due to the formation of this oxide whose thicknesses were estimated from such changes, using the molar volume ratio (2.4) of Ta_2O_5/Ta. Such estimates were linearly proportional to Electron Microprobe determined O contents. The Ta_2O_5 thickness (equivalently, mass) was found to increase with the square root of total time at peak temperature for thinner oxides grown up to 500 C (see Figure 3). These results are expected for a diffusion controlled process and agree with constant oxidation temperature findings. Above ≈ 600C, the rate becomes linear with time due to excessive stress effects and a breaking off of the Ta_2O_5 layer. Profilometry measurements show that excessive roughening accompanies linear oxidation, as expected.

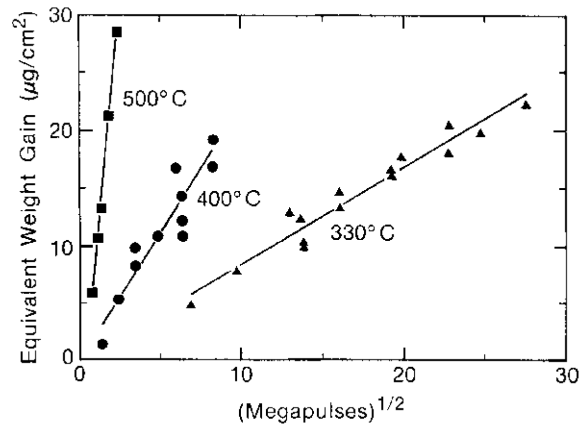

Figure 3. Weight gain of β-Ta films due to oxidation vs total cycles for 5 microsecond pulses.

Typical AES depth profile data are shown in Figure 4. Similar data taken on α- and β-Ta films show that the latter contain less oxygen after equivalent oxygen exposures, thus supporting the idea that the latter offers superior passivation. Overall, these results suggest that β-Ta is to be preferred over the α-Ta phase for passivation—assuming other features (e.g., grain size and stress) are equivalent. Note also that peak temperature should be kept below 600C to prevent a loss of passivation.

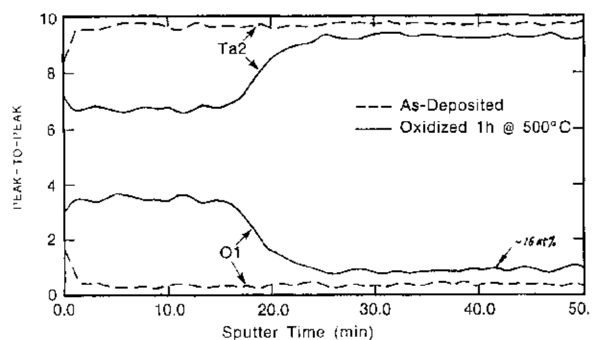

Figure 4. AES compositional depth profiles of β-Ta films, as-deposited and after oxidation.

Further improvements in device lifetime can be achieved by protecting the Ta against oxidation with a noble metal.[14] This approach uses a total of 4 passivation layers: two dielectrics and two metals, the top being a noble-like metal. The duplex dielectrics virtually eliminate pinholes[15] which would allow the metal overcoat to contact the resistors, leading to electrochemical corrosion. In addition to providing electrical isolation, the dielectrices must be: thermally-conducting; hard to resist cavitation: chemically inert should voids in the metal overcoats be present; have excellent conformal coverage to the resistive network; and, reasonable thermal expansion coefficients. The top metal overcoat should be noble, hard, ductile, high-melting, chemically-inert, cavitation-resistant and have moderate stress levels, at most. Ruthenium, rhodium, rhenium and palladium films meet these criteria. The lower metal overcoat should have similar features except it would not be a noble metal and must also provide excellent adhesion to the adjacent films. The total overcoat thicknesses must be kept reasonably small to prevent failure due to cracking, delamination and thermal fatigue, in addition to degrading device performance by allowing excessive thermal spreading of the heat pulses.

As one example of this approach, Ru/β-Ta overcoats were added to Si_xC_{1-x}:H/Si_xN_{1-x}:H passivated heaters and assembled into ink jet devices which were jetted in *certain inks* up to 800 MC with no significant loss of Ru or Ta oxidation as detectable by AES depth profiling and other techniques. One could extrapolate these results and estimate that devices passivated with Ru/Ta or similar metallurgical materials could survive several billions of firing cycles. In the absence of Ru, the Ta_2O_5 thickness would be on the order of 100nm with substantial O concentrations near the Ta/carbide interface and device failure would be expected to follow not long thereafter. An important caveat. Such noble metal/Ta passivations do not invariably yield a *lifetime* head since the ink itself can drastically alter device reliability. In another ink test, excessive kogation occurred resulting in unacceptably large fluctuations in drop velocity and premature device failure because of runaway thermal effects after only tens of millions of firings. The origins of this effects are not understood although noble metals are known to possess high catalytic activity which may thereby cause ink components to decompose in some fashion or other. Clearly the lifetime of a particular overcoat system depends on a totality of printhead factors.

Conclusions

We have presented here evidence demonstrating cavitational and oxidative distraction of Si_xC_{1-x}:H and β-Ta passivation films. These materials deteriorate mainly due to oxidation which can be aided by stirring provided by cavitation. The Ta top overcoat seems to be quite adequate for a lifetime head but can be further improved by a noble metal overcoat. A number of factors interact to determine the rates of overcoat failure including: materials; processes; geometries; and, ink compositions.

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