NOVEL AMORPHOUS METAL THIN FILMS FOR MEMS APPLICATIONS

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ABSTRACT

Thin film materials development has been critical to modern advances in electronics and Micro Electro Mechanical Systems (MEMS). This present work focuses on the development of advanced amorphous metal thin films for applications in Thermal Ink Jet (TIJ) devices; one of the earliest developed and most commercially successful MEMS devices to date. Collaboration between the printing division of Hewlett-Packard (HP) and Oregon State University (OSU) to develop amorphous metal thin films for thermal ink jet devices has resulted in remarkable progress toward development of thin film amorphous metals capable of handling extreme thermal and chemical shock. These results have been achieved by utilizing typical vacuum deposition processes known to be scalable into a manufacturing environment.

INTRODUCTION

Amorphous metal materials have been in bulk commercial production for years, incorporated into golf clubs, tennis rackets, and more recently rumored to be under investigation for incorporation into Apple products through collaboration with Liquidmetal Technologies [1]. In MEMS, amorphous TiAl₃ in Texas Instruments DLP technology stands at the forefront of commercialization of thin film amorphous metal materials [2]. Work on this class of materials continues as a research area for MEMS and electronic devices due to the advantageous atomically smooth surface, mechanical stability, and chemical resistance imparted to them by their amorphous, grain boundary free structure [3, 4].

A TIJ firing event creates one of harshest thermal, mechanical, and chemical environments in the world at the heater surface. By instantly flashing a thin layer of water into steam to eject a drop of aqueous based ink, extreme thermal stress is introduced as well as thermally initiated corrosion. One of the most damaging events occurs when the steam bubble collapses creating a micro jet cavitation event as depicted in Figure 1.

Figure 1: Diagram of Mechanical Damage Due to Microjet Cavitation [5]

Huge engineering efforts have been conducted by HP over more than two decades to protect the central heater element from failure as millions of ink drops are fired over the lifetime of a printhead. This engineering effort has recently enabled HP to release the world's fastest desk top printer: Figure 2 – the Office Jet Pro X. This printer contains more than 42,000 micron scale nozzles across ten MEMS die. Each nozzle has a rated lifetime of several million

actuators and must reliably perform over the lifetime of the printer.

Figure 2: Image of HP Pro X Page Wide Printer and Printbar Containing 10 TIJ MEMS Die.[6]

Materials work completed several years ago by HP resulted in the formation of an as deposited amorphous metal based on Cobalt and Chromium alloyed with other materials. Figure 3 demonstrates that we were able to create a high quality, dense thin film with excellent adhesion to the substrate layers. However, Figure 3 also demonstrates that the system did not survive initial thermal shock testing; testing resulted in crack propagation into the substrate and device failure.

Figure 3: SEM Micrograph and Optical Image of Early HP Attempt at Using a Mechanically Tough Amorphous Alloy – Failure in Thermal Shock Testing

The collaboration with OSU builds upon this foundation and greatly expands the technical depth of the materials design. The current material of focus is based on sputtered TaWSi with additional dopants.

RESULTS AND DISCUSSION

Experimental Approach

At the launch of the project Oregon State University completed an exhaustive search of the scientific literature looking for information on the thin film amorphous metals and leveraging extensive literature for bulk metallic glasses.

From the literature OSU formulated the following materials design guidelines for creation of a thermally stable amorphous metal:

- The material should *be composed of three or more different elements with refractory metals* accounting for ~70% of the total composition.
- The components should have a *wide distribution of atomic radii*, with at least a 12% difference in size between any two components.
- There should be a *large negative heat of mixing* among each of the components.
- At least one of the component components should be a *metalloid* such as Si.

Starting with these guidelines a number of materials compositions were selected for testing. Ta was used as a central material in the majority of the compositions investigated because it is known to perform well in a thermal ink jet device.

The compositions were created using sputter deposition from two inch and three inch targets at an approximately four inch target to substrate spacing. The targets were fabricated using standard pressed powder techniques by various vendors. Both RF and DC power delivery were investigated for the appropriate deposition conditions with DC power delivery being generally more desirable to increase deposition rate of the thin film. Various power conditions were utilized up to about 150 Watts DC on a three inch target. Process pressures were investigated from 1mT to 20mT on three different sputter deposition platforms.

Thin Film Characterization:

To determine if the materials are suitable for the harsh environment of a thermal ink jet ejection event we devised a series of materials characterization experiments to understand the capability of the different materials. We focused primarily on thermal stability and resistance to chemical reaction as the initial variables of interest.

Thermal Stability

The thin film materials stack directly in contact with ink must heat to more than 250°C on a time scale of micro seconds to achieve proper steam drive bubble for precise ejection of ink. This places an enormous stress on the thin films during firing. This thermally induced stress can be greatly exacerbated when elements of the thin film stack change morphology through grain growth or other structural conversions commonly activated in a high temperature environment. Ta has performed well for many years in thermal ink jet devices with reasonable stability enabled by the refractory nature of the material. Even though Ta is fairly thermally stable it is still susceptible to structural changes through tens of millions of firing events demanded for baseline reliability by modern TIJ printers. Of the several amorphous metal materials investigated we found a blend of TaWSi provides the most promising thermal stability.

Most vacuum deposited metal thin films are formed in a crystalline phase. Figure 4 provides an example of an as deposited crystalline Ta thin film commonly used in a TIJ device. The columnar structure of the crystalline Ta grains can be clearly observed in Figure 4. The boundaries between the grains provide increased surface area for chemical attack and a dislocation point increasing the probability of mechanical degradation of the Ta thin film during operation of a TIJ device.

Figure 4: SEM of Cleaved Ta Cross Section

Figure 5 provides a Transmission Electron Microscopy (TEM) micrograph and electron diffraction image of TaWSi from OSU's imaging facility demonstrating that the TaWSi was amorphous as deposited. The TEM image indicates that the TaWSi is a high quality, dense thin film with good adhesion to the underlying thermally grown Silicon Oxide substrate. The diffuse rings in the electron diffraction image indicate that the materials are amorphous as deposited.

Figure 5: TEM Cross Section with Electron Diffraction of a TaWSi Amorphous Metal Thin Film: as Deposited

The TEM analysis results of a sample heated at 300°C in air for one hour are provided in Figure 6. The annealed TaWSi sample exhibited evidence of minimal surface oxidation, but the bulk of the film remained as an amorphous metal.

Figure 6: TEM Cross Section with Electron Diffraction of a TaWSi Amorphous Metal Thin Film Heated in Air at 300°C

An investigation using TEM Energy Dispersive X-Ray Spectroscopy (EDS) was performed on the sample to verify that the oxidation was restricted to the surface of the thin film. Figure 7 provides an example of the EDS data collected. Careful review

of the EDS data confirms that the bulk of the film is a homogeneous mixture of TaWSi with oxygen restricted to the surface of the thin film. This is consistent with the film being high density and free of grain boundaries, additionally confirming the possible benefits for this material set in a prolonged high temperature oxidizing environment.

Figure 7: TEM – EDS imaging of TaWSi Thin Film Annealed in Air for One Hour.

Chemical Resistance

The volume of water flashed to steam is so small in TIJ devices that even human cells have been reliably jetted with this technology.[7] However rapid heating of a small volume of an aqueous solution to several hundred degrees Celsius can cause chemical reactions to be initiated that do not occur under more standard conditions. When firing a device millions of times low probability chemical reactions can have a significant impact on the materials used for the heater – ink interface. For initial materials screening HP performs reliability testing in inks under more standard conditions; if any material degradation is observed under these conditions the material is not considered suitable for integration into a TIJ device. In this case careful analysis of oxidation behavior was also conducted to verify stability of the film stack at high temperature.

Chemical resistance was investigated by oxidizing the TaWSi in air and exposing it to relevant HP ink chemistries. The TaWSi materials demonstrated excellent resistance to oxidation and chemical attack in HP ink. Figure 8 provides a comparison of Ta and TaWSi thin films heated under the same experimental conditions to 600°C in air. Based on the previously discussed Ta cross section and the TEM imaging of TaWSi we believe the completed failure of Ta heated to 600°C is related to oxidation of the thin film at the grain boundaries. Oxidation at the grain boundaries leads to in plane volume expansion of the thin film, significant in plane stress build up, and eventual failure of the Ta thin film. The TaWSi did demonstrate buildup of a surface oxide, but failure of this film was not observed until heated in air to temperatures in excess of 850°C. Additional investigation of surface oxide formation at 300°C by ellipsometry revealed that the surface oxide of Ta and TaWSi both terminated between 5nm and 10nm, further supporting the hypothesis that grain boundary oxidation plays a significant role in failure of the Ta film heated in air.

Figure 8: Optical Images Showing Complete Failure of Ta and Stable TaWSi Amorphous Metal Thin Films Heated to 600°C in Air.

Bench top testing with ink using standard reliability testing conditions revealed no significant difference between Ta and TaWSi. The resistance to chemical attack in ink, thermal stability, and oxidation resistance provided the technical support required to justify construction of a TIJ device using the TaWSi thin film in contact with ink during firing.

Materials Stability During TIJ Firing Event

The TaWSi passed initial blanket film test, but questions regarding stability through a harsh TIJ firing event still remained. A test chip was created to evaluate the thin film materials for adhesion, stability under thermal stress, chemical resistance, and resistance to cavitation. The parts were fired with a pool of ink or water on their surface. This is commonly referred to as a pond test and is designed to deliver the maximum cavitation damage possible. Figure 9A is a tilted view SEM micrograph of a TIJ firing element after more than 100,000 actuations in water. From this image we see that the thin film stack is mechanically stable through the firing events as no delamination of the thin films is present. Some cavitation damage was observed, Figure 9B, after exposure to the extreme cavitation environment.

Figure 9: SEM Micrograph of Fired Resistor – A. Circle Identifies location of Cross Section in Figure 9 - Damage Not Visible at This Magnification. B. Magnification of region shown in image A.

Figure 10 provides SEM cross sections comparing the thin film performance in a TIJ firing event for Ta and TaWSi. Both materials demonstrate good adhesion to the substrate and general film integrity through the TIJ firing events. The pitted regions towards the center of each image of Figure 9 were created through cavitation events. From this cavitation information we can conclude that both demonstrate similar cavitation damage under the given harsh cavitation test conditions.

Figure 10. SEM Cross Section of Ta vs. TaWSi Fired Resistors Showing Stable Thin Films and Cavitation Damage

Additional testing was completed using ink to determine resistance to chemical attack through repeated TIJ firing events. No strong differentiation was observed between Ta and the TaWSi thin films of comparable thickness.

All of the testing indicates that TaWSi is likely to perform well in a long lifetime TIJ device. However, at the time of writing this paper, additional work will be required to understand if the amorphous TaWSi is capable of providing a true disruptive advantage in a production TIJ printer environment.

CONCLUSIONS

Research into the design and creation of novel amorphous metal thin films has been completed. We have successfully demonstrated amorphous metal thin films capable of withstanding extreme thermal shock and chemically aggressive environments.

The following conclusions can be made for the TaWSi materials set.

- An amorphous, grain boundary free TaWSi was successfully sputter deposited. The thin film remained amorphous even at high temperatures for extended time in an oxidizing environment.
- The TaWSi materials set demonstrated significantly improved thermal stability relative to Ta when heated to high temperatures in an oxidizing environment. The amorphous metal film did not fail until a much higher temperature than Ta. It also demonstrated the ability to act as an intrinsic barrier to bulk oxidation of the thin film.
- The TaWSi passed all early stage ink based reliability testing with relevant HP inks.
- Testing in a harsh TIJ cavitation environment revealed that the thin film adhesion and cavitation resistance of the TaWSi are at least as good as that observed for a default Ta thin film.

Amorphous TaWSi performed very well in short lifetime TIJ device testing. Successful long life testing more relevant to product will be required if the materials are to be moved into manufacturing for HP printers.

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