GEOTHERMAL ENVIRONMENTAL EXPOSURE TESTING OF ENCAPSULANT AND DEVICE MATERIALS FOR HARSH ENVIRONMENT MEMS SENSORS

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ABSTRACT

The development of harsh environment sensors for down hole geothermal well monitoring is needed to both optimize current production wells and to develop more accurate subsurface mapping to reduce the cost of well exploration. Exposure testing of encapsulant and device materials must be conducted within harsh environments to determine material survivability in the well bore environment. Mass change and sputter XPS chemical analysis were conducted on silicon, sapphire, silicon carbide (SiC), and aluminum nitride (AlN) after up to 100 hours of exposure testing in water at its critical point.

INTRODUCTION

Devices such as harsh environment temperature, pressure and telemetry sensors (accelerometers and gyroscopes) are of high interest for the optimization of geothermal well performance. It has been predicted that enhanced geothermal energy systems (EGS) and hydrothermal systems have the potential to provide up to 200,000 exajoules at 100,000 MW within the next 50 years [1]. Achieving this goal is aided by the implementation of sensors within new and existing wells to collect temperature and pressure data. The development of these sensors requires testing of harsh environment materials in high temperature and pressure water conditions. Once water reaches the critical point and enters the supercritical regime, the liquid and gaseous properties of water become more destructive due the volatility of the free OH^- and H^+ ions.

In addition to the high temperature and pressure of the harsh geothermal brine environment, low pH rapidly leads to sensor degradation and thus poor sensor reliability. For this initial set of tests, water, rather than brine, is used for sensor exposure to establish a baseline. Robust sensor packaging, Figure 1, is required to facilitate



Figure 1: Schematic image of encapsulated MEMS sensor. Harsh environment encapsulation protects MEMS sensors from corrosion and oxidation in geothermal wells.

sensor survivability for long duration well monitoring. While many studies have been conducted to determine the corrosion rates of sintered and CVD SiC in supercritical water [2-6], none of these studies investigated crystalline 4H-SiC, sapphire, or AlN, all of which are harsh environment MEMS materials which may be useful for encapsulation or device layers. While it was not expected that AlN would survive the critical point water, by exposing the AlN thin film, we learn about the AlN survivability within the harsh environment in the event of encapsulation failure.

In this paper, we report the results of exposure testing of 4H-SiC, sapphire and sputtered AlN on SiC in water at its critical point. This data can be used in materials selection when designing sensors for down-hole operation.

MATERIALS SELECTION

For this study, three harsh environment materials were selected. These materials, whose properties are summarized in Table 1, were chosen for their high temperature survivability and chemical resistance. Their high bond energy is high compared to that of the Si control sample used in the experiment. All of these materials would have a little to no oxidation at the tested 374°C. However due to the free ions in critical point water, local oxidation and corrosion may degrade the samples at this lower temperature by exceeding the materials bond energy. Bond energy is as indicator of corrosion resistance, however, other factors including the materials physical composition (single-crystalline versus poly-crystalline), defect density, and surrounding environment chemistry also play a role in determining corrosion chemistry and rates.

Material	Chemical Bond Type	Bond Energy at 25 °C (kj/mol)	Melting Temperature (°C)
Sapphire	Ionic/Covalent	595.65 ⁷	2050
4H-SiC	Covalent	318 ⁸	2830*
AlN	Covalent	279.8 ⁹	2470
Silicon	Covalent	222 ⁸	1420
*SiC Sublimation Tomporatura			

Table 1: Summary of Tested Materials Properties

*SiC Sublimation Temperature

EXPERIMENTAL PROCEDURE

We are reporting data from four different sample types prepared for testing. Two different single crystalline 4H-SiC wafers from CREE Inc. were used for the exposure tests. C-axis sapphire wafers from MTI corporation were purchased and diced. Highly oriented caxis AlN was reactively sputtered on a 4H-SiC wafer using an Endeavor AT radial multi-chamber sputter system. AlN was chosen as the device layer material to expose as it is a high temperature, piezoelectric material used to telemetry sensors. Finally, <100> n-type Si based sample with AlN and patterned platinum was used as a control for the exposure tests.

These materials were diced to size (approximately 5 mm by 5 mm) and weighed on a scale with 5-point Mettler balance with 10 micrograms accuracy. They were then mounted in stainless steel (SS 316) holders during exposure to critical point water. Steel filler rods were placed behind the sample holder to keep the holder at the end of the vessel and to reduce the volume of critical point fluid.

A simulated geothermal environment was achieved using a Tuttle-type pressure vessel, Figure 3. This vessel has an inner diameter of $\frac{1}{4}$ " (6.35 mm) allowing for the exposure of 5mmx5mm dies. The vessel is closed using a conical sealing method and connected to a water pressure line. The pressure line pressure sets the pressure of the fluid within the vessel at a given temperature. The temperature controller thermocouple is recessed into the vessel at the closed end. This allows for monitoring of the temperature closer to the samples precise location within the test setup. The pressure vessel is made of waspaloy, a Ni rich metal, which results in the intrusion of Ni from the vessel walls into the water. As most geothermal wells are cased with steel, the Ni contamination could be common in geothermal wells. This contamination allowed for the depth analysis of Ni intrusion into the material layers.



Figure 3: Tuttle-type pressure vessel used to simulate geothermal well conditions for exposure testing.

Tests were conducted at 374°C and 22 MPa which corresponds to the critical point of water. The samples were exposed for 1, 5, 20, 50 and 100 hours. Up to six tests were run in parallel by locking off individual vessels from the pressure line post pressure check. To ensure constant pressure when isolated from the pressure line and thus the pressure gage, individual vessels were not isolated until leak checks were performed and the oven temperatures had stabilized. Each vessel was reconnected to the pressure line at the internal pressure of that vessel to ensure proper final pressure before disconnecting it from the system. The vessels were then quenched in water baths before sample removal.

The holders were removed from the vessel and the samples were removed. Before recording the final mass, the samples were dipped into a clean water bath, an ethanol bath and then dried on a hot plate. This was done to remove any large particles sitting on, but not attached to, the samples surface.

RESULTS

The mass was measured before and after the exposure test to examine any macroscale changes in the materials. As the mass of the AIN is within the tolerance of the scale, the SiC data points should show similar mass loss results for those samples. The silicon control samples experience a mass loss of over 20% over 100 hours of exposure as shown in Figure 4. The mass of the AIN and Pt was subtracted from the initial masses as the Pt delaminated as the AIN eroded in the vessel. This is a linear mass loss trend which indicates that there is a constant etching and removal of Si from the sample surface. It is most likely that the Si is being oxidized by the free ions seen in water at its critical point. This oxide then requires less energy to be removed from the sample surface into the surrounding water.



Figure 4: Mass change of silicon carbide, sapphire, and Si based samples for 1 to 100 hours of testing.

There was no detectable mass change of the SiC or sapphire samples over the 100 hours of exposure. This indicates that either there is very little damage done to these samples or that the damage did not cause a significant mass change as it may be causing a change to the material structure but not etching it away.

The macroscale sample damage can be seen in Figure 5. Both the SiC and sapphire samples surfaces have some vessel residue on their surfaces. This residue was removed with an ethanol bath. The Si sample lost the Pt and AlN and the silicon also begins to corrode. This degradation is most visible in the upper right corner of the sample.



Figure 5: (Top) Before images of expose 5x5mm samples. (Bottom) Images of samples post 5 hours exposure in critical point water. Note: The sputtered Pt delaminated from the AlN layer on the Si sample during exposure.

Sputter XPS analysis was conducted to determine the degradation of the SiC, sapphire and AlN over the exposure times. Surface scans of the SiC samples showed the expected Si, O₂ and Ni binding energies, however there was also a carbon peak. Looking at the specific carbon bonding showed carbon as it is known to be found with SiO₂, the formation of hydrocarbons and the diffusion of Ni, Figure 6. The exact chemistry of the hydrocarbon formation is now entirely clear, however, it is likely that the free ions in the critical point water caused local reactions with the SiC to form SiO₂ and C. Both the out diffusion of oxidation reaction products and product removal are hindered by the surrounding static water more than that of the traditional oxidation vapor stream. This would lead to the buildup of products within the sample. Thus, we do not see the clean SiO₂ layer as predicted by the theoretical modeling of the SiC oxidation process. These free carbon atoms are shown in the scan in elemental form, however they also achieved a more stable state in the form of larger molecule chains when bonding with free hydrogen ions. The silicon carboxide would also be formed in a similar way with the addition of some silicon atoms.



Figure 6: Surface XPS data of 100 hour exposed SiC sample. Analysis of the C1s carbon peak, upper left, revels that there is oxidation as well as the formation of hydrocarbon chains.

Once surface damage was detected, the depth of that damage was measured. While some material degradation is tolerable for an encapsulation or substrate material, that damage must be asymptotic to prevent total encapsulant failure. To determine the depth of sample degradation, the samples were sputtered in 5, 10 and/or 15 nm depth increments. The sputtering depth rate was calculated based on the sputtering rate of SiO₂. The hydrocarbons, elemental carbon, and silicon carboxide were only found on the surface, or first 10 nm, of the samples. However, the SiO₂, and the Ni contamination continued through the SiC sample. At each depth step, an XPS scan was taken. The strength of the Ni and SiO₂ signals decreased with depth into the sample. The oxide depth was determined to be reached when the signal was indistinguishable from the scan noise. Over the 100 hours, the oxidation behavior reached an average depth of approximately 150 nm from the surface of the SiC samples, as seen in the depth scans shown in Figure 7. The sample exposed for 50 hours only showed oxidation to 65 nm. This non-asymptotic behavior indicates that the SiC will continue to degrade with increased exposure time. Nickel ions were able to penetrate to a depth of 50 nm in the SiC after 100 hours of exposure. This was an increase of 15 nm from the 35 nm Ni penetration depth with the 50 hour exposed SiC sample.



Figure 7: Depth of oxidation of SiC over 100 hours of testing based on XPS of the O1s peak. The peak is indistinguishable from the signal noise by 150 nm.

The degradation of the sapphire structure was shown in a different way from that of SiC. As sapphire is already an oxide, the XPS scans were looking for binding energy shifts in the oxide peak. These shifts around the 74 eV binding energy for the $Al_{2}p$ peak indicate oxide degradation to a different binding from $Al_{2}O_{3}$ to other aluminum oxide forms. The binding energy shift can be seen in Figure 8. This damage by the infiltration of ions penetrated to a depth of 50 nm for both 50 and 100 hour exposure tests. The nickel diffused to a depth of 10 nm for both of these exposure times. This indicates that sapphire was the most stable encapsulation material for down-hole geothermal sensors.



Figure 8: Shift in Al2p peak from a 50 hour sapphire sample. The first 50 nm of the sample are degraded and shown by a shift in the peak. All of the peaks have been shifted by 9 eV to account for sample charging.

While down-hole devices will be encapsulated during operation, it is useful to know the survivability of potential device layers in the event of partial encapsulation failure. The 100 nm AlN thin film layers that were exposed to the simulated geothermal environment did not survive for long exposure times. Over the 100 hours of exposure, the AlN layer showed an exponential decay in thickness, as would be expected with chemical etching, Figure 9.



Figure 9: AlN thin film degradation over 100 hours of testing. An exponential decay trend line is shown with the experimental data.

CONCLUSIONS

The exposure data detailed in this work provides the basis for the design of fabrication processes with encapsulation to shield sensors during down-hole operation in geothermal wells. Of the materials exposed, sapphire is the most promising material for both substrate and encapsulation of MEMS devices for down hole operation because there is no additional material degradation between the 50 and 100 hour exposure tests. While SiC does not appear to have a asymptotic degradation behavior, longer duration tests may show that degradation ceases at a deeper depth than the sapphire samples. Both longer duration tests of SiC and exposure testing of more potential device layer materials must be conducted to gain a more comprehensive understanding of MEMS materials within the down-hole geothermal environment.

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