HIGH TEMPERATURE MATERIALS FOR THIN-FILM THERMOCOUPLES ON SILICON WAFERS

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ABSTRACT

We are developing an instrumented calibration wafer for radiometric temperature measurements in rapid thermal processing (RTP) tools for semiconductor processing. The instrumented wafers has sputter deposited thin-film thermocouples to minimize the thermal disturbance of the wafer by the sensors. The NIST calibration wafer also employs platinum-palladium wire thermocouples to achieve a combined standard uncertainty of 0.4 °C in temperature measurement of the thin-film thermocouple junction at 900 °C. The high temperatures of the wafer has required the development of new thin-film material systems. We report the results of our testing and characterization of sputtered platinum, palladium, rhodium, and iridium thin films using titanium bond coats on thermally oxidized silicon wafers. Depth profiling with secondary ion mass spectrometry was used to determine the diffusion profiles from the metal film to the silicon after heat treatments as high as 1000 °C. Electron microscopy and optical microscopy were used to follow reactions and the deterioration of the thermoelectric films. In addition, performance tests up to 1000 °C in the NIST RTP test bed were used to determine the stability of the material systems. Failure mechanisms and limitations of the thin-film thermocouple materials are discussed with data on hysteresis and drift in thermometry performance. The results of our evaluations indicate that Rh/Ir thin-film thermocouples have the best properties for wafer temperatures above 900 °C.

INTRODUCTION

Improved temperature measurement is a critical need in rapid thermal processing (RTP) of electronic circuits. The RTP tool is normally monitored by radiometric temperature measurements which are subject to uncertainties due to variable emissivities and reflected radiation. The most effective way to reduce the uncertainties of these radiometric measurements is to calibrate them on line in the RTP tool. Thermocouple instrumented wafers have been used for making these calibrations in RTP tools. These calibration wafers and some of the thermocouple materials have been described previously, [l - 3]. At NIST we are exploring the use of thin-film thermocouples on the wafer [2] in order to minimize the thermal perturbation caused by the temperature sensor. The NIST calibration wafer includes Pt/Pd wire thermocouples which extend to the periphery of the wafer allowing temperature measurement standard uncertainties of less than 0.1 °C at their measuring junction [4] and we use thin-film differential thermocouples from the platinum/palladium (Pt/Pd) junction to the wafer calibration location. With temperature variations of 10 °C or less across the wafer,l the surface temperature of the wafer at the thin-film thermocouple junction can be measured with a standard uncertainty of 0.4 °C [5]. These uncertainties have been established with calibration tests of the Pt/Pd wire thermocouples and rhodium-platinum (Rh/Pt) thin-film thermocouples on the International Temperature Scale of 1990 (ITS-90) [6]

The Pt and Pd thin films that were evaluated previously had limited stability at the higher temperatures for RTP radiometer calibration (900 °C to 1000 °C). The work discussed in this paper is intended to clarify the causes of limitations of the Pd and Pt thin films and

report the evaluation of suitable thin films for higher temperature operation. In choosing the materials for thin-film sensors on silicon wafers, the key factors are the chemical and mechanical interactions between the films and the wafer and between the thin films and the environment. Since we need a temperature sensor which can be used at temperatures up to 1000 °C in a rapid thermal processing tool, the stability of the interfaces between the films and the wafer are the most critical. At these high temperatures thin-film thermocouples have advantages over thin-film resistance thermometers since they are not sensitive to mass changes which affect resistance. The key factor in thermocouple stability (and also necessary for resistor stability) is uniform composition of the electrically conducting phase. Stress level and other metallurgical factors such as grain size and defect population have a smaller effects on the Seebeck coefficient. Reactions with oxygen from the atmosphere or solid phases, compound formation with nearby solid constituents, or diffusion to and from nearby phases all can cause drift in the thermoelectric output and the Seebeck coefficient of the thermoelements. Because thin films inherently have short diffusion distances, these reactions cause instabilities at lower temperatures than the instabilities observed with wire thermocouples. At 1000 EC, the use of alloy thermocouples is practically precluded because of preferential reactions of their constituents. For example, thermocouples with thermoelements of platinum-rhodium alloys exhibit appreciable drift due to preferential oxidation of rhodium at 700 EC to 900 EC [7].

For application in high temperature calibrations, the thin-film thermocouple is joined to a wire thermocouple for use up to 1000 EC. The best connection between them is a welded

connection to survive high temperature service. Such welded junctions are more difficult with compounds such as the silicides and nitrides which have been used for thin-film thermocouples [8] and metallization on silicon. These compounds form oxides on the surface which interfere with the thermoelectric circuit. Therefore, pure non-reactive elements appear to be the best choice for this application. Although gold and silver may be useful at low temperatures, their low melting points eliminate them from serious consideration at 1000 EC. Platinum, palladium, rhodium, and iridium appear to be logical choices for low reactivity and high temperature capability. These metals are also tolerant of partial pressures of 10^{-5} atm (1Pa) of oxygen or water vapor which are commonly present in production environments. They enable the construction of a more durable calibration wafer. We have also investigated the use of tungsten and rhenium thin-film thermocouples on the silicon wafers but they have been found to be too sensitive to oxidation to be useful in this application.

EXPERIMENTAL PROCEDURE

Silicon wafers of 200 mm diameter were obtained with a thermal oxide of 300 nm to 320 nm thickness. Some of these wafers were diced to form 50 mm x 10 mm test coupons for use in thermal treatment and calibration experiments. They were cleaned with acetone and alcohol, rinsed in deionized water, and irradiated with 193 nm radiation for uv-ozone cleaning. Typically, the coupons were sputter coated in 0.4 Pa of 99.999 % Ar after a pump down to 10^{-4} Pa. The first coat of material to bond to the silicon dioxide was a layer of 7 nm to 10 nm thickness made from a titanium target of 99.995 % purity. This

bond coat was followed by a coating of 0.3 Φm to 1.0 Φm thickness of platinum (99.99 %), iridium (99.9 %), rhodium (99.95 %) or palladium (99.97 %). The array of thin-film thermocouples on calibration wafers included two measuring junctions at 16 mm from the center of the wafer 11 mm apart and two measuring junctions 50 mm from the center 62 mm apart. The Pt/Pd wire thermocouples were welded to the thin-film weld pads 10 mm from the edge of the wafer. A more complete description of the calibration wafer and its use can be found in reference [2].

High temperature tests were conducted in controlled atmospheres using an alumina tube furnace, a fused silica tube calibration furnace [5], and the NIST RTP test bed [2]. Resistance measurements were made using a standard 4 point resistance tester. Scanning electron microscopy (SEM) was performed on an Hitachi S4000 at a working distance of 16 mm with an Oxford 6566 x-ray analyzer [9]. Secondary ion mass spectrometry (SIMS) was performed on a CAMECA IMS4F [9] using O_2 + bombardment at 8.0 Kev impact energy with detection of positive secondary ions. Calibrations of thin-film thermocouple elements were conducted using the NIST thin-film thermocouple calibration cell [10]. RTP cycling and calibration tests were performed in the NIST RTP test bed [2]. Adhesion tests were made using a Sebastian [9] tab pull tester.

RESULTS

The thin-film thermocouple materials were evaluated using both long duration (2 h to 20 h) exposure in a controlled atmosphere tube furnace and in the NIST RTP test bed

which permits rapid thermal cycling. These tests were used to determine whether any problems could be expected during applications as a calibration wafer for RTP. We expected problems such as oxidation or reaction of the thin film with its atmosphere, reaction between the thin film and the silicon wafer, reactions with the Ti bond coat which can lead to loss of adhesion, and coalescence of the films due to self diffusion. One of the simplest ways of detecting changes in the film's thermoelectric properties was to measure its resistance. A change in resistance could result from a change in resistivity, which would indicate a change in its thermoelectric properties, or a loss of material to vaporization or reactions which would not affect the thermoelectric properties. Changes such as recrystallization, oxidation, inclusion precipitation, porosity, and delamination are well detected by optical and electron microscopy. Interphase diffusion is best detected by depth profiling with SIMS and SEM X-ray compositional analysis. Since adhesion of the films in this application is critical, we chose to test this property directly. We also report on lifetimes in the RTP tool and the stability of thermoelectric properties in a thin-film thermocouple calibration test.

Palladium films

We have reported previously on the limitation of Pd thin-films [3]. The most sensitive test relates to the drift in emf at 880 °C of 9 % in 24 h for a 0.7 μm thick film and more serious drift at higher temperatures. Although RTP calibration applications would rarely require exposures that long, the practical limit for the Pd films is probably close to 850 °C for films less than l μm thick. Figure 1 is an SEM image of a 0.7 μm Pd film

annealed at 900 °C for 2 h. This film shows large (3 μm) pores and excessive grain growth with faceting after recrystallization. SIMS depth profiling on the as-deposited 0.7 μm thick Pd film clearly showed the boundaries Pd/Ti and Ti/SiO_2 with enhancement of the signal where oxygen was present as expected. After annealing for 2 h at 700 °C or at 800 °C the Ti signal was broadened significantly but it remained centered around the interface. Ti has very little solubility in Pd [10] and the broadening of all three signals (Ti, Pd, and Si) may be related to pore formation, and surface roughening.

Platinum

Platinum has a higher melting point (1773 °C) than Pd (1550 °C) and does not oxidize in air above 450 °C. It is used in commercial wire thermocouples and Pt-67 [5] is the reference standard maintained by NIST. The Pt/Pd wire thermocouple has a Seebeck coefficient of approximately 18.2 μV/K at 900 °C. The calibration of a sputtered 0.5 μm Pt film on the Si wafer up to 950 °C versus Pt wire and the unexpected results of its 1 μV/K to 2 μV/K emf was reported previously [3]. This test indicated very low hysteresis (< 1%) on rapid cooling compared to the output on heating. The Pt films are also subject to coalescence. In addition, at 900 °C and above, Ti becomes more soluble [10]. Figure 2 is the SIMS depth profile of a 0.7 μm thick Pt film with Ti bond coat on a Si wafer with 310 nm of thermal oxide after a 2 h exposure in N_2 at 900 °C. The migration of Ti through the Pt film to the exposed surface (t = 0) is evident. Notice the enhancement of both the Ti and Pt signals near the surface due to oxygen enhancement, which was not evident in the as-deposited sample. This oxygen presence is probably due to TiO_2

forming on the exterior surface. The migration of the Ti was also evident to a lesser extent on a sample annealed at 630 °C. Diffusion of the Ti to the surface also leads to a weakening of the bond between the Pt film and SiO_2.

The loss of Ti at the interface and the increase of the diffusion coefficients of Pt above 900 °C led to a coalescence problem in Pt films. Figure 3 is an SEM image of a 0.4 µm thick Pt film held at 1000 °C in N_2 for 2 h indicating severe pore growth, loss of adhesion, and surface roughening. The circular pores in figure 3 are 1 µm to 3 µm in diameter. We saw similar pores optically at 2000x in a 0.3 µm thick Pt film on a calibration wafer which was thermally cycled 44 times for calibration runs. The last cycle reached 1011 °C and it caused failure of the thin-film thermocouple.

Rhodium

Rhodium (Rh) has a higher melting point (1966 °C) than Pt and correspondingly lower diffusion coefficients at 1000 °C. Rh is not like Pt or Pd which have a yield stress of near 30 MPa at room temperature, but like Ir, has a yield stress more than ten times that of Pt. The Young's modulus of Rh (≈300 x 10^9 Pa) is also twice that of Pt. Therefore, Rh and Ir (which has even higher moduli and yield stress) will be stressed primarily in the elastic region on thermal cycling in contrast to Pd and Pt which deform plastically at these temperatures. Rh_2O_3 is stable in air up to approximately 900 °C and therefore we performed all testing in an N_2 (O_2 = 2 Pa) atmosphere.

SEM analysis at 10 000X displayed a recrystallization and coarsening of the 0.4 μm thick Rh film after 2 h at 1000 °C (figure 4). The recrystallization is also highly facetted and 2 μm wide pores are visible in figure 4 at the triple grain boundary intersections. X-ray compositional analysis of the film after the 1000 °C exposure revealed a small Si signal (3% of the peak height of the Rh signal) from the pores but no Ti was observed.
SIMS depth profiling of the Rh thin film after 2 h at 1000 °C [figure 5] displayed a spreading of the Ti, Si, and Rh signals compared with the as-deposited signals. This indicates roughening of the surface and probably some interphase diffusion but it has less movement of Ti than with the Pt sample. Similar patterns, but to a lesser degree, were observed for Rh films after heat treatments at 750 °C and 900 °C.

A calibration of the thermoelectric emf of a Rh film 0.4 μm thick film versus Pt is given in figure 6 showing both heating and cooling curves which have less than 0.6 % hysteresis between 875 °C and 975 °C. The indications are that the Rh films are very stable at these temperatures. Very little damage was apparent on the Rh films of the calibration wafer heated to 1011 °C. The Rh films also had excellent adhesion (> 30 MPa) after annealing in N_2 at 1000 °C for l h. The resistivity of Rh films was found to be 5 μΩcm (u = 1 μΩcm, k = l) after a 900 °C anneal in N_2 compared to the bulk value 4.6 μΩcm [11] and the as-deposited value of 6 μΩcm.

Iridium

Iridium thin films bonded to the thermally oxidized Si wafer with Ti are very stable at 1000 °C. Ir, as previously mentioned, has one of the highest elastic moduli, a very high yield stress, a high melting point (2440 °C), and low self-diffusion coefficients at 1000 °C. With a thermal expansion coefficient mismatch of 3×10^{-6} K^{-1} compared to Si, the expected residual stresses on cooling from 1000 °C would be elastic-compressive as is true with Rh. Oxidation rates are slow in air up to near 1100 °C where the vapor phase of IrO_3 forms. We heat treated the Ir films in N_2 (O_2 = 2 Pa) and SIMS depth profiling indicated some Ti migration to the outer surface but most of the Ti remained near the Ir/SiO_2 interface after 2 h at 1000 °C. An SEM image of a 0.3 μm thick Ir film is presented in figure 7. The Ir has recrystallized after 2 h at 1000 °C and has deep grain boundary grooving and facetting on crystal planes. The black spots, which are approximately 0.25 μm in diameter, are the result of the early stages of self diffusion and coalescence. No Si or Ti signal was visible on the X-ray analysis leading to the conclusion that the pits in figure 7 do not reach the Si or that they are so small that the X-ray signal cannot escape through the 0.3 μm thick Ir film. The resistivity of the Ir films was 6 μΩcm (u = 1.5 μV/K, *k* =1) after a 900 °C anneal in N_2 compared to the as-deposited 11 μΩcm and a handbook value for bulk Ir of 5 μΩcm [11].

The Ir thin film versus Pt calibration up to 980 °C, figure 8, illustrates the excellent hysteresis of less than 0.1 % in heating and cooling from 850 °C to 980 °C. The Seebeck coefficient of the film vs Pt in this range averages 14.5 μV/K with an uncertainty of

0.4 µV/K (k =1) compared to the Rh film which was 18.7 µV /K, u = 0.5 µV/K (k =1). These results would yield an output of 4.2 µV/K in the 850 °C to 980 °C range for the thin-film thermocouple Rh/Ir. Adhesion of the Ti bonded 0.4 µm Ir film after 2 h at 1000 °C in N_2 was greater than 50 MPa.

CONCLUSIONS

Pure elements have advantages over alloys and compounds because of selective reactions of the constituents in alloys which produce drift in the thermoelectric output. Previous work with alloys [7] and silicides [8] has explored the properties of these materials. We also prefer the thermoelements which are least sensitive to oxidation rather than W and Re, as reported above, because of problems associated with residual oxygen and water vapor which are often present in RTP chambers.

Platinum-palladium thin-film thermocouples on silicon wafers have a high thermoelectric output (≈16 µV/K), but if the films are less than 1 µm thick the practical limit for their use as an RTP calibration wafer is approximately 850 °C, with brief excursions up to 900 °C. The Pd leg is more sensitive to degradation by pore growth, coalescence, and delamination. Pt thin films have similar problems at 950 °C to 1000 °C. Some modifications would make the films more refractory: e. g. increasing the thickness, adding a grain growth inhibitor such as an insoluble precipitate, and covering with an oxide can retard coalescence.

Both Rh and Ir thin films appear to be very stable in this application at temperatures up to 1000 °C. Both Rh and Ir thin films have very low hysteresis versus Pt and excellent repeatability in thin-film thermocouple calibration tests. The optical microscopy, SEM, SIMS depth profiling, and stability of resistance of the films confirm their suitability for this application. No evidence of silicide reactions with any of the sensor materials indicated that 300 nm of thermal oxide on the silicon was an adequate diffusion barrier.

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FIGURES

1. Pd film on Si wafer, 0.3 µm thick, annealed 2 h at 900 °C. Notice pore growth and large facetted grains. Bar is 6 µm.

2. SIMS depth profile of 0.6 µm thick Pt film with Ti bond coat after 2 h at 900 °C. Ti has migrated to the surface and oxidized.
3. SEM image of 0.4 µm thick Pt film after 1 h at 1000 °C. Small pores are 0.1 µm to 0.3 µm in diameter and the film has lost adhesion. Bar is 100 µm.
4. SEM image of 0.4 µm thick Rh film after 2 h at 1000 °C. Recrystallized grains are facetted and have 2 µm wide pores. Bar is 4 µm.
5. SIMS depth profile of 0.4 µm thick Rh film after 2 h at 1000 °C.
6. EMF of Rh thin film versus Pt as a function of temperature.
7. SEM image of 0.3 µm thick Ir film on wafer with 0.25 µm diameter pits. Bar is 10 µm.
8. EMF of Ir thin film versus Pt as a function of temperature.