Titanium Nitride for MEMS Hotplates

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Abstract—**Titanium nitride (TiN) has been investigated as a material for MEMS hotplate heaters operating at high temperatures. The material is IC compatible and can be sputtered with different residual stresses. This increases the mechanical strength of the membrane. Stress is mainly lowered by increasing the nitrogen pressure during the sputtering. Low stress TiN (+0.1 GPa) shows a resistivity which is 40 times higher (3.3 mΩ cm) than that of high stress TiN (81 μΩ cm, -16.4 GPa). In addition, the temperature dependence of the resistivity is smaller, less linear, and changes from a positive to a negative value after a burn in cycle. The observed differences can be explained from the grain structures of the materials. Low stress TiN contains much more voids between the grains than high stress TiN. When heated, TiN should be protected against oxidation by a passivation layer.**

Keywords— **MEMS heater, hotplate, TiN thin films, sputtered films, stress, resistance, TCR.**

I. INTRODUCTION

The MEMS hotplate is a basic component of many gas sensors because of its low power consumption and cost-effective manufacturing. A hotplate often consists of a membrane of low stress SiN with a resistive heater in the middle [1,2]. The temperature is derived from the resistance change of the heater. Usually, the heaters are made of Pt or poly-Si. These materials, however, do not operate reliably above 550ºC. This is because in many materials the grain boundaries start to diffuse above one-third of the melting point. As a result, residual stresses relax [3]. Heaters for temperatures higher than 550ºC. have been made of Ta_5Si_3 [3]. This material, however is not so widely available.

A material similar to Ta_5Si_3 is titanium nitride (TiN). It combines a very high melting point (2950ºC) with a low electrical resistivity (down to 20 μΩcm [4]). Thin layers of TiN are widely used in CMOS processes as a diffusion barrier for metals. Therefore, it has been proposed for heaters in general [5]. For hotplate heaters, it has two additional advantages. It can be made with any desired residual stress, increasing the strength of the membrane. In addition, it has a very moderate heat conductivity (15 $Wm^{-1}K$ for bulk material). This leads to low conductive losses through the connecting wires.

We have investigated high and low stress TiN with respect to the following properties: resistivity, temperature coefficient of resistance (TCR), and behaviour at high temperatures (≥830ºC). Finally, we relate the properties to the deposition conditions and the morphology of the grain structure.

II. EXPERIMENTAL

Hotplates as well as separate heaters are fabricated on a (100) Si wafer; see Fig. 1 and 2. The wafer is coated with 500 nm of LPCVD low stress SiN. Then, a 10nm thick Ti adhesion layer followed by 200 nm of TiN is deposited by reactive sputtering in a Trikon Sigma d.c. magnetron reactor.Two different recipes were used: the standard recipe with high residual stress and a low stress recipe (see Table 1). The stress in the TiN is determined from the wafer curvature measured with a Tencor FLX2908. The sheet resistance is measured with a four-point prober.

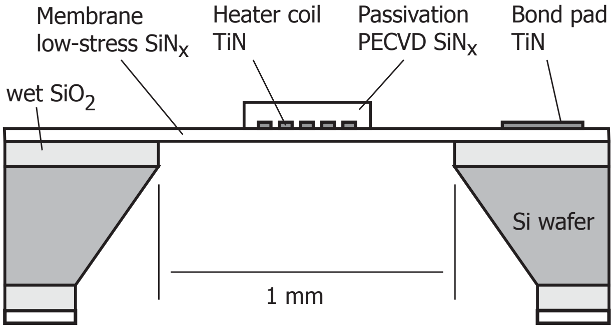

Figure 1. Schematic cross section of the hotplate.

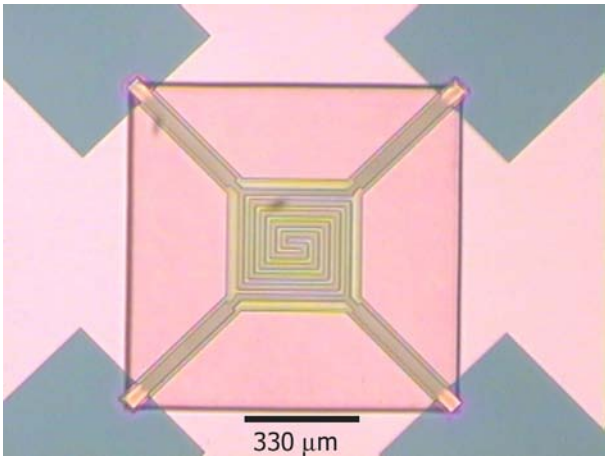

Figure 2. Optical image of a TiN hotplate heater coil.

The TiN is patterned by dry etching in a Trikon Omega plasma etcher. The etch recipe is similar to the one used to etch Al. The end point of the etching is detected by monitoring the spectral emission line of Ti at 335 nm.

The thickness of the transparent SiN is determined before and after etching using a Leitz MV-SP spectrophotometer. The thickness of the Ti/TiN stack is determined by measuring the step height with a Tencor Alphastep profilometer. The wafers with the hotplates are passivated with a layer of PECVD SiN. The silicon substrate is locally etched away in a KOH solution to form the (1x1 mm) membrane of SiN.

The electrical resistance of the TiN is determined with a Cascade semi automatic probe station and an Agilent source monitor system. The probe needles are made of tungsten carbide and have a tip radius of 5 µm. The system is also used for internal heating of the hotplates. The temperature dependence of the resistance is determined for the separate heaters by external heating and cooling of the chuck of the probe station between -50ºC and +200ºC. The temperature behavior of the hotplate resistance is estimated from the dissipated power during internal heating of the spiral heater.

Table 1. Main parameters used for TiN sputtering, for the high and low stress layers.

	High stress	Low stress
N_2 part. press.	0.41 Pa	1.8 Pa
Total pressure	0.53 Pa	2.3 Pa
Power	12 kW	0.5 kW
Bias voltage	0 V	0 V
Temperature	350ºC	350ºC

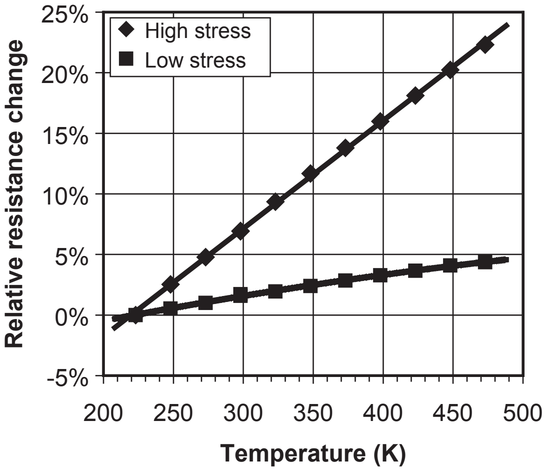

Figure 3. Resistance change as a function of temperature for a high stress and a low stress TiN heater.

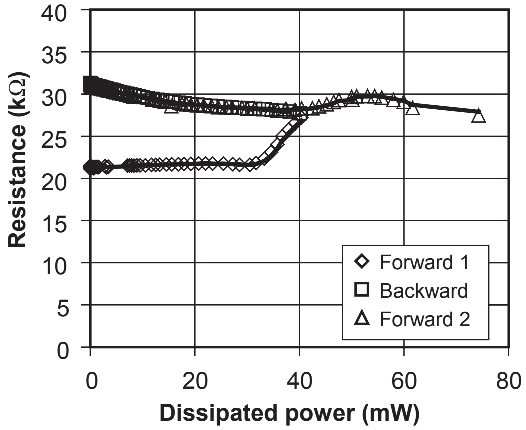

Figure 4. Resistance of a hotplate heater as a function of dissipated power, for heating to 40 mW, cooling down, and heating again. Material: low stress TiN. The curve of 'Backward' coincides with the 'Forward 2' curve.

Some wafers with separate heaters are annealed at a temperature of 830ºC for one hour to test the residual effects on the adhesion of the TiN to the SiN, the stress, and the sheet resistance. This is done in the curvature meter under a flow of N_2, and in a Lenton 16/75/610 tube furnace under a flow of Ar. Both systems cannot be pumped to vacuum levels.

The grain structure of the TiN layers is examined with a Transmission Electron Microscope (TEM), an FEI CM30T.

III. RESULTS

As deposited, the color of the low stress TiN is reddish, and that of the standard, high stress TiN is between gold and copper. The residual stress in the standard layers is very high: -16.4 GPa, whereas it is only +0.1 GPa in the low stress layers. The etch rate in the plasma is 0.32 µm min^{-1}, with a selectivity of 2.0 to the SiN. No difference in terms of etch rate is observed between low and high stress TiN. The average overetch is 20 nm and the decrease in uniformity is 4 nm.

The resistivities of the materials are very different: 81 μΩ cm for the high stress material and 3.3 mΩ cm for the low stress material. The influence of the temperature on the resistances is plotted in Fig. 3 for external heating and cooling.

According to the plots, the resistance is almost linearly increasing at this temperature interval. The TCR at room temperature of high stress material is 8.3×10^{-4} K^{-1}, and that of low stress material is 1.9×10^{-4} K^{-1}. The temperature dependence of the resistance of high stress material has the highest linearity. After the temperature cycles on the chuck no hysteresis is observed.

However, irreversible changes in the resistance are observed during internal heating of the hotplates with low stress TiN. This burn in effect is shown in Fig. 3. The resistance increases rapidly when more than 30 mW is dissipated, and continues to increase during cooling down to the starting temperature. Renewed heating, however, follows the cooling curve. As a result, the TCR of this new, stable curve has changed from a positive to a negative value. Heating above 75 mW is destructive.

A special property of the TiN layers is that they have a high contact resistance with the probe needles. Acceptable resistance values are only reached after a short voltage pulse. This pulse causes small imprints on the layer, which are not observed after a normal mechanical contact with the probe needles.

The examination with the TEM reveals grain structures which are very different for low and high stress TiN. As shown in Fig. 4, high stress material consists of densely packed fibrous grains with a typical width of 10 nm. The structure corresponds to Zone T of the Thornton classification [6,7]. Low stress material, on the other hand, has a porous structure of fibrous grains and contains many voids. Dark field images indicate that the grain size is also around 10 nm. The grain structure corresponds to Zone 1 of the Thornton classification.

The anneal at 830ºC destroys heaters which are unpassivated. Although the TiN does not show adhesion problems, it can no longer be contacted electrically. TEM inspection shows that new grains are formed which have a different shape and electron diffraction pattern. No changes are observed, however, in the heaters with a passivation layer of PECVD SiN. A disadvantage of this layer is its cracking at high temperatures.

IV. DISCUSSION

The differences in the macroscopic properties of the low and high stress TiN can be explained to a large extent from the morphology of the grain structures. These, on their turn, can be related to specific sputtering conditions. In a general sputtering process, the distinction between the formation of grains of Zone 1 and Zone T is made by a combination of gas pressure and substrate temperature [6,7]. Above a given inert gas pressure (1 Pa at 350ºC) the surface diffusion of adatoms is impeded. This can be attributed to an increasing oblique component of the incident gas atoms flux, developing into hemispherical incidence [7]. The reduced surface diffusion increases shadowing effects and promotes the creation of voids.

The presence of voids relaxes residual compressive stress. Stress is also decreased by low sputtering powers when the ion bombardment of the layer is low [8]. Both conditions apply to our low stress material.

The resistivity of our high stress TiN, 81 μΩ cm, is relatively low compared to many other values reported in literature [4, 11]. Nevertheless, it is three times higher than the minimum value of 20 μΩ cm [4]. This minimum value is found for stoichiometric TiN layers, which have a golden yellow color. The copper color of our material indicates that it is slightly nitrogen rich [9]. This is coherent with the relatively high nitrogen pressure during deposition [10]. Low resistivity values are also found in materials which are free of oxygen contamination [10,11]. This can be reached by applying a bias voltage below -75V to the substrate during sputtering. Our TiN has been sputtered at a bias voltage of 0V.

The resistivity of our low stress TiN, 3.3 mΩ cm, is quite high. Nevertheless, for our bias voltage and nitrogen pressure similar values have often been reported [4,11]. The high resistivity mainly arises from the voids in the microstructure. Voids lead to loosely connected grains which impede the charge transport. It can also be said that the charge carriers experience a high surface scattering on the grain boundaries.

The critical temperatures of the hotplate can be estimated from the dissipated power and from measurements on devices with a similar geometry [2]. The irreversible resistance change starts at 30 mW, corresponding to about 180ºC. The destructive heating occurs at 75 mW, which roughly corresponds to 400ºC.

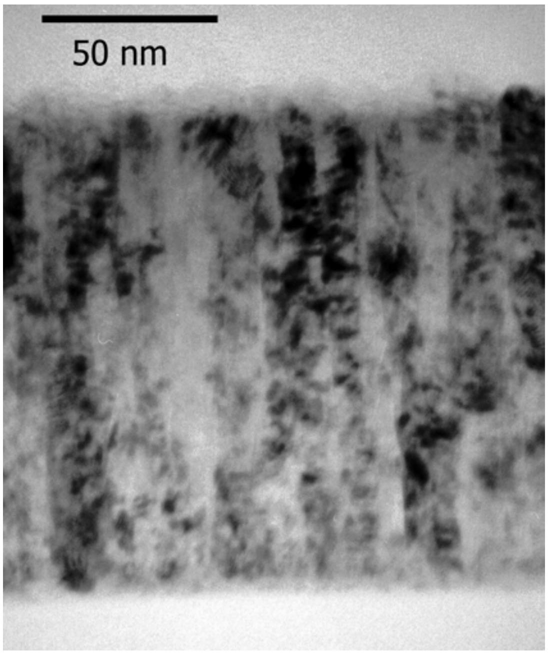

Figure 5. TEM cross sections of the high stress TiN layer.

The hysteresis of the resistance with increasing temperature has only been reported in Ref. [12], for TiN deposited by CVD. It occurs above 300ºC, together with a negative temperature coefficient. In our case it occurs above 180ºC. The change of sign of the TCR after burn in complicates the use of the heater in a feedback system.

The difference in temperature behaviour between low and high stress materials could well be caused by the measure in which the grains contact each other. A resistivity which increases linearly with temperature corresponds to metallic behavior, whereas a decreasing, nonlinear resistivity corresponds to semiconducting behavior [12]. Probably both conduction mechanisms are present in the TiN. Metallic conduction occurs within the grains and semiconducting conduction occurs across the grain boundaries. In polycrystalline silicon, these boundaries have been shown to act like energy barriers for the charge carriers [13]. Charge transport across the barriers occurs by thermionic emission. In low stress TiN the grain boundaries are probably loosely attached to each other and therefore dominate the total resistance value. The grains in the high stress TiN, on the contrary, are densely packed. The boundary resistance can then be low compared to the resistance within the grains.

The high resistance of unpassivated TiN after the annealing is probably caused by oxidation. An oxidation model from literature predicts that 200 nm of TiN is consumed within one hour when the temperature exceeds 450ºC [14].

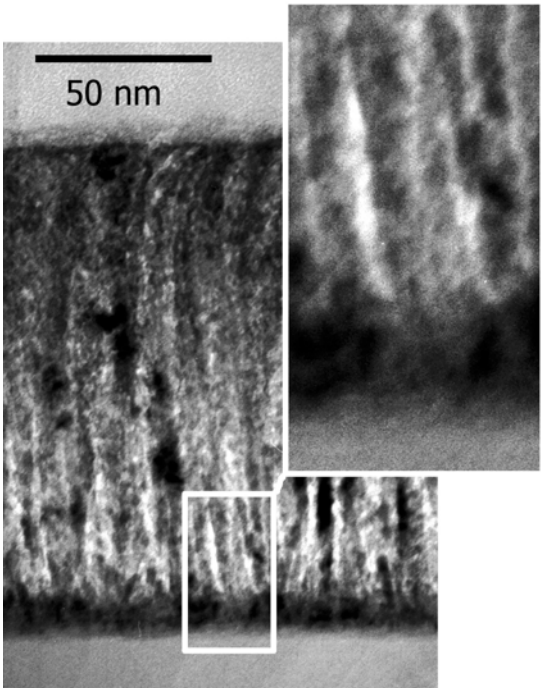

Figure 6. TEM cross sections of the low stress TiN layer. The white lines are void, showed enlarged in the inset.

V. CONCLUSIONS

Hotplate heaters of TiN have been fabricated and characterized. The residual stress in the TiN layer can be decreased by adjusting the sputtering parameters, especially by increasing the gas pressure. This, however, leads to an entirely different morphology of the grain structure. This increases the resistivity by a factor 40. It also yields a low TCR, which becomes nonlinear and negative after burning in. The TiN should be covered with a passivation layer to prevent oxidation.

ACKNOWLEDGEMENTS

This research is supported by the Technology Foundation STW, Applied Science Foundation of NWO and the technology programme of the Ministry of Economic Affairs. We would like to thank Emile van der Drift, Frans Tichelaar and Patricia Kooyman for the helpful discussions, and the members of the DIMES Technology Centre for their help with the processing.

REFERENCES

[1] J.M. Gardner, S.M. Lee, P.N. Bartlett, S. Guerin, D. Briand, and N.F. de Rooij, *Digest of Transducers 2001*, Munich, Germany, 2001.

[2] D. Briand, A. Krauss, B. van der Schoot, U. Weimar, N. Barsan, W. Göpel, and N. F. de Rooij, Sens. Actuat. B 68 (2000) pp. 223-233.

[3] A. Pollien, J. Baborowski, N. Ledermann, and P. Muralt, *Digest of Transducers 2001*, Munich, Germany, 2001.
[4] N. Kumar, P. Pourrezaei, M. Fissel, T. Begley, B. Lee, and E.C. Douglas, J. Vac. Sci. Technol. A 5 (1987) 1778-1782.
[5] P. de Moor, A. Witvrouw, V. Simons, and I. de Wolf, *Proceedings of SPIE*, Santa Clara 3874 (1999) 284-293.
[6] M. Ohring, *Material science of thin films, deposition and structure,* Academic Press, San Diego, 2002.
[7] S. Craig and G.L. Harding, J. Vac. Sci. Technol. 19 (1981) 205-215.
[8] F. Vaz, P. Machado, L. Rebouta, P. Cerqueira, Ph. Goudeau, J.P. Rivière, E. Alves, K. Pischow, and J. de Rijk, Surf. Coat. Technol. 174-175 (2003) 375-382.
[9] M. Wittmer, J. Vac. Sci. Technol. A 3 (1985) pp. 1797-1803.
[10] G. Lemperière and J.M. Poitevin, Thin Solid Films 111 (1984) 339-349.
[11] J.-E. Sundgren, Thin Solid Films 128 (1985) 21-44.
[12] J.-F. Lei, H. Okimura, and J. O. Brittain, Mater. Sci. Eng. A123 (1990) 129-140.
[13] P.J. French and A.G.R. Evans, Solid St. Electron. 32 (1989), 1-10.
[14] M. Wittmer, J. Noser, and H. Melchior, J. Appl. Phys. 52 (1981) 6659-6664.