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PROPERTIES OF THIN FILMS FOR HIGH TEMPERATURE FLOW SENSORS

By

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Summary

Properties of thin film materials and substrates are analysed for application in a high temperature flow sensor. Temperature sensitivity of the film sensor is the product of thermal coefficient of resistance and resistivity, $\alpha\rho$ and can be maximized by proper choice of materials. It is shown that silicides of transition and refractive metals are ideal materials to achieve a high value of $\alpha\rho$. These materials are stable up to $1000\,^{\circ}C$. The frequency response of the sensor increases with the ratio of the thermal conductivities of the film and the substrate, k_f/k_s. This ratio is also high for the silicides on many common substrates. Intrinsic semiconductors of high bandgap materials have a high value for α and are suitable for high temperature operation. SiC and diamond are two candidate materials. Their thermal conductivities are also high. Since diamond film has the highest known thermal conductivity, a high frequency response is expected from a diamond film sensor. The choice of substrate materials is limited to quartz and Al_2O_3 when low thermal and electrical conductivities are required. The choice is also based on matching the thermal expansion coefficients of the substrates with those of the deposited film so as reduce the film stress. Thin film deposition and patterning techniques for silicide, SiC, and diamond are identified and discussed briefly.

1. Introduction

Thin films have a large ratio of surface area to mass. This is useful to design devices with high frequency response and large signal to noise ratio for many applications. A hot-film anemometer is such a device used in measuring skin friction coefficient and detecting transition regions in fluid flow. NASA Langley has developed such sensors for boundary layer transition at both ambient and cryogenic temperatures.[1] Thin metal films of Cr and Ni are deposited on insulating layers such as SiO_2 and parylene C. The sensor assembly could be directly deposited on metal models or could be inserted in the model. The properties of the thin film materials currently used in such sensors are adequate only for ambient or low temperature measurements. For high temperature applications above $500^{\circ}C$, appropriate materials are to be identified which meet several requirements.

2. Theory

2.1 Temperature Sensitivity

The resistance of metals increases with increase in temperature; however this variation also depends on the temperature of operation. A general formula for resistance variation with temperature is given as

$$R = R_0 [1 + \alpha_1 (T\text{-}T_0) + \alpha_2 (T\text{-}T_0)^2 + \alpha_3 (T\text{-}T_0)^3 +...] \qquad (1).$$

In equation (1), R and R_0 are the resistances at temperature T and T_0 respectively, and α's are the thermal coefficients of resistance. The values of α in the higher order terms are generally several orders of magnitude smaller than α_1 and hence often neglected. Therefore the temperature sensitivity for the first order approximation is given by,

$$(dR/dT) = \alpha R_0 = \alpha \rho_0 L/A \qquad (2),$$

where ρ_0 is the resistivity at at T_0, L is the length, and A is the area of cross section of the thin film sample. Hence $\alpha \rho_0$ can be regarded as a parameter to be maximized for the selection of thin film materials for an ideal flow sensor. For metals, the resistance

increases with temperature and α therefore, will be positive.

In the case of an intrinsic semiconductor, the resistivity ρ is given by

$$\rho = [\, N_i \, e \, (\mu_e + \mu_h) \,]^{-1} \qquad (3),$$

where e is the electronic charge, μ_e and μ_h are respectively the mobility of electrons and holes. The intrinsic carrier concentration N_i given by

$$N_i = N_e = N_h = 2\,[\, 2\pi kT/h^2\,]^{3/2}\, [m^*{}_e/m^*{}_h]^{3/4} \exp(\,-E_g/2kT) \qquad (4),$$

where N_e and N_h the concentration of electrons and holes, $m^*{}_e$ and $m^*{}_h$ are their effective masses, E_g is the bandgap of the semiconductor, k is the Boltzmann's constant and h is the Planck's constant. Therefore, from equation (3),

$$\alpha = (1/R)\,(dR/dT) = (1/\rho)\,(d\rho/dT) = -\,(1/N_i)\,(dN_i/dT) \qquad (5).$$

Using equation (4), equation (5) becomes,

$$\alpha = -\,(\,3/2T + E_g/2kT^2) \qquad (6).$$

In equation (6), the temperature dependence of mobility and energy gap is omitted.

α is negative for intrinsic semiconductors. For large bandgap semiconductors, both α and ρ will be large; hence the product $\alpha\rho$ and the temperature sensitivity can be maximized.
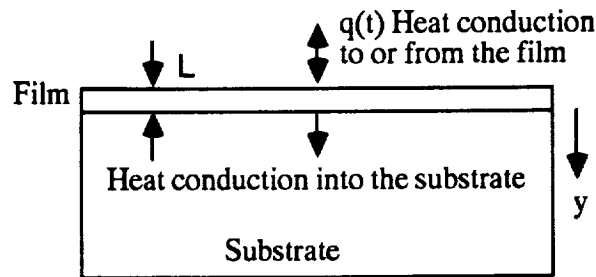
2.2 Frequency Response

Figure 1. Thin film on a planar substrate.

Detailed analysis of the frequency response of thin film sensors were carried out by Vidal[2] and Lowell and Patton.[3] Vidal used a planar geometry for analyzing the sensor having a film deposited on a substrate as shown in Figure 1.

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By considering the time dependent rate of heat transfer from the film to the substrate, one can write the heat equations for the film and the substrate. For the film medium, $0 \le y \le L$,

$$\frac{\partial T_f}{\partial t} = \frac{k_f}{\rho_f c_f} \frac{\partial^2 T_f}{\partial y^2}$$

(7).

For the substrate medium, $L \le y \le \infty$,

$$\frac{\partial T_s}{\partial t} = \frac{k_s}{\rho_s c_s} \frac{\partial^2 T_s}{\partial y^2}$$

(8).

In equations (7) & (8), t is the time, T is the increment of temperature at time zero, k, ρ and c are the thermal conductivity, density and the specific heat with subscripts f and s for the film and the substrate respectively. The boundary conditions for each case are:

$$t \le 0, T_f(y) = 0$$

$$t \ge 0, y = 0,$$

$$\frac{\partial T_f}{\partial t}\Big|_{y=0} = -\frac{1}{k_f} q(t)$$

and

$$t \le 0, T_s(y) = 0$$

$$t \ge 0, y = L, T_f(L) = T_s(L)$$

$$k_f \frac{\partial T_f}{\partial t}\Big|_{y=L} = k_s \frac{\partial T_s}{\partial t}\Big|_{y=L}$$

$$\lim_{y \to \infty} T_s = 0$$

We have used equations (7) and (8), and similar boundary conditions to determine the thermal diffusivity of the substrate and thin film materials.[4] By employing Laplace

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transformations, general equations for T_f and T_s can be obtained. Additionally if we make the following three assumptions: (1) the film thickness L is small, (2) the thermal conductivity of the film is higher than that of the substrate, i.e., $k_f >> k_s$, and (3) the product $\rho_f c_f$ is small for a fast response, the solution for the surface temperature for $y = 0$ can be obtained as,

$$T(t) = \frac{1}{\sqrt{\pi k_s \rho_s c_s}} \int_0^t \frac{q(\lambda)}{\sqrt{t-\lambda}} d\lambda - \frac{2}{\sqrt{\pi k_f \rho_f c_f}} \sum_{n=1}^{\infty} \sigma^n \int_0^t \frac{q(\lambda)}{\sqrt{t-\lambda}} \left\{ 1-e^{-\frac{n^2 L^2 \rho_f c_f}{k_f(t-\lambda)}} \right\} d\lambda$$

(9).

In equation (9), λ is an integration variable and

$$\sigma = \frac{\sqrt{\dfrac{k_f \rho_f c_f}{k_s \rho_s c_s}} - 1}{\sqrt{\dfrac{k_f \rho_f c_f}{k_s \rho_s c_s}} + 1}.$$

Equation (9) contains two terms, the first represents the surface temperature of the substrate alone while the latter is due to the presence of thin film on the substrate. When L is very small, the higher order terms of the second term in equation (9) can be neglected and the approximate solution for the surface temperature can be written as

$$T(t) = \frac{1}{\sqrt{\pi k_s \rho_s c_s}} \int_0^t \frac{q(\lambda)}{\sqrt{t-\lambda}} d\lambda - q(\lambda) \frac{L}{k_f} \left(\frac{k_f \rho_f c_f}{k_s \rho_s c_s} - 1 \right)$$

(10).

Equations (9) and (10) will be identical if k_f is large, and L and k_s are small.

The maximum frequency of response of the sensor is related to $(k_f / \rho_f c_f L^2)$. It is imperative to use a thin film material of high k_f to achieve a high frequency response. Similar conclusions were drawn from a more detailed theoretical analysis by Lowell and Patton.[3] Various structures considered are shown in Fig. 2.
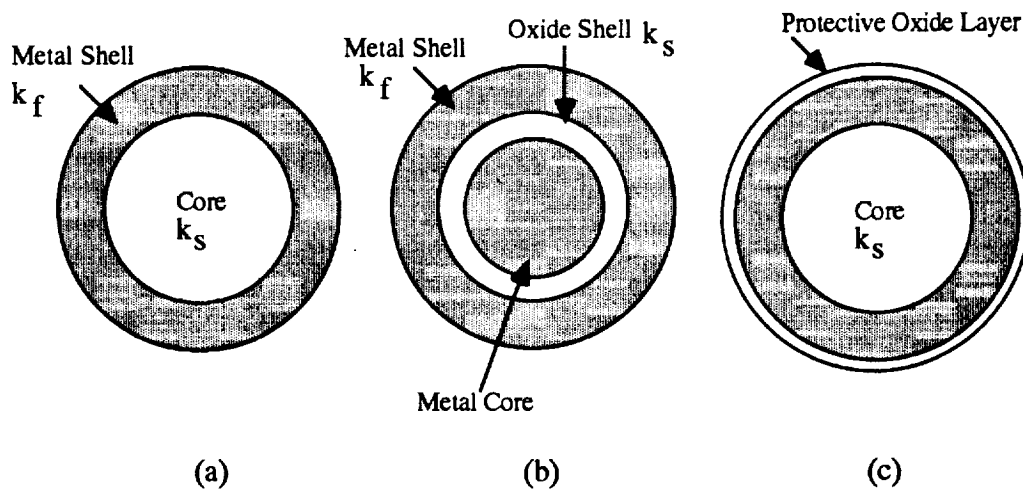
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Figure 2. Various models of shell structures used by Lowell and Patton; the core and the shell are analogous to the substrate and the film in figure 1. (a) metal shell on an insulator core, (b) metal shell and metal core separated by an insulator shell, and (c) similar to (a) with a protective insulating layer.

For fast response the temperature changes in the shell must be faster than that of the core. This is achieved by decoupling the thermal effects of the shell from the core by using high thermal conductivity ratio k_f/k_s. The variation of frequency response with k_f/k_s is given in detail by Lowell and Patton. The structure shown in Fig. 2(c) is especially suitable for high temperature operation of the sensor where the insulating layer protects the film from adverse environment.

3. Materials for High Temperature Sensors

The thin film materials and substrates suitable for sensors can be selected on the basis of the requirements given in section 2. The product $\alpha\rho$ of the thin film sensor element should be high for a high temperature sensitivity. The ratio k_f/k_s must be made large to enhance the frequency response. Therefore the substrates must have a low thermal and electrical conductivity.

Nickel is a common thin film material used in many sensor applications. In this section we make a comparison of the properties of Ni with those of several other materials which might be considered as candidates for high temperature applications. One such group of materials is silicides, formed alloying silicon with an appropriate metal. In Table 1, the values of ρ, α, the product $\alpha\rho$, and k_f are compared.

Table 1
A comparison of the properties of metals and their silicides

Material	Resistivity ρ $\mu\,\Omega\text{-cm}$	TCR α $^oC^{-1} \times 10^{-3}$	$\alpha\rho$ $(\Omega\text{-cm/}^oC) \times 10^{-9}$	k_f W/cm ^oC
Ni	6.3	6.7	42.2	0.95
$NiSi_2$	60	3.3	198.0	~0.84
Cr	12.9	3.0	38.7	0.91
$CrSi_2$	142	2.9	411.8	~0.84
W	5.4	4.8	25.9	1.78
WSi_2	70	2.9	203.0	~0.84
Ti	43	4.7	202.1	0.22
$TiSi_2$	25	4.6	115.0	~0.84
Ta	12.6	3.8	47.9	0.54
$TaSi_2$	50	3.3	165.0	~0.84
Mo	5.1	4.1	20.9	1.38
$MoSi_2$	100	6.4	640.0	~0.84
V	24.8	2.8	69.4	0.6
VSi_2	55	3.5	192.5	~0.84
Zr	41.0	4.4	180.4	0.22
$ZrSi_2$	40	1.3	52	~0.84

All silicides except $TiSi_2$ and $ZrSi_2$ have higher resistivity compared to the corresponding metals. The thermal coefficient of resistance α, is positive and in general lower than the values for the metals. Hence silicides behave like metals, having a high value of $\alpha\rho$,

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leading to a higher temperature sensitivity. In terms of composition, the silicides usually contain 90% Si. The thermal conductivity of Si is lower than that of most metals; therefore the silicides have approximately the same thermal conductivity as Si, as shown in the last column of Table 1. Silicides have high melting points similar to those of their respective metals and they are quite stable in oxidizing ambient up to about 1000 °C.

Among the semiconductors of large bandgap, SiC and diamond are two candidate materials. Their properties are compared with those of Si in Table 2.

Table 2

Relevant Properties of Semiconductors

Material	Bandgap (eV)	TCR α ($^\circ$C^{-1})	k_f (W/cm $^\circ$C)
Si	1.1	-0.075	0.84
SiC	3.0	-0.198	4.9
Diamond	5.5	-0.36	20

The intrinsic resistivity of SiC and diamond at room temperature, are several orders of magnitude higher than the value for Si. However, they can be doped to have a range of values from 0.1 to 100 Ω-cm. In each case, the product $\alpha\rho$ will be several orders of magnitude higher than the values listed in Table 1 for metals and silicides. Perhaps, diamond has the highest thermal conductivity of any material and SiC also has a high k_f.

The choice of substrate material is based on its low value of thermal conductivity so that the ratio k_f/k_s is enhanced to achieve a high frequency response, as discussed in section 2. Two obvious candidate materials are quartz (k_s = 0.125 W/cm $^\circ$C) and Al_2O_3

(k_s = 0.376 W/cm ^oC). For diamond film on quartz, k_f/k_s is 160, which is perhaps the highest value for sensor which should exhibit high frequency response. In addition, the choice of substrate is dictated by their surface properties and thermal expansion coefficients. These properties will make the deposited thin films adhere well. The expansion coefficients of the thin film and the substrate must be identical to reduce stress in the deposited film to a minimum. Quartz and Al_2O_3 satisfy these criteria and have already been used as substrates in hybrid microelectronics.[5]

4. Deposition and Patterning Techniques

4.1 Silicides

Silicides can be formed by the two common methods: evaporation and sputtering. Though chemical vapor deposition (CVD) can also be used, it is often limited by the availability of suitable volatile compounds required for the CVD process. A metal film can be deposited on silicon or polysilicon or a composite of metal and silicon can be deposited on any substrates by using evaporation or sputtering. For coevaporation two separate sources are required as the silicide source compound decomposes near its melting point. Cosputtering of metal and silicon can be from two separate targets or from a hot pressed silicide targets. In each case, following the deposition the silicide formation is completed by a high temperature sintering process around 900 ^oC. These source materials are readily available from most manufacturers of high purity electronic materials.

4.1.1 Evaporation

Evaporation of the materials can be carried out in vacuum by resistive, induction, electron bombardment (E-beam) or laser heating. Since the metals involved in silicides have high melting points, E-beam evaporation is the most common method of deposition. Two separate E-beam sources are used for coevaporation. The rate of evaporation is controlled from each source to obtain the required ratio of metal to silicon in the silicide. The radiation damage induced by the E-beam will be removed completely during the

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sintering process. Since E-beam evaporation is carried out in a high vacuum condition, the deposited films are generally as pure as the source used. Silicides prepared by this technique is used in the fabrication of VLSI devices.[6]

4.1.2 Sputtering

A composite silicide target is often used for RF and DC magnetron sputtering. Cosputtering or layer by layer sputtering of metal and silicon targets is also used for the film deposition. As in the case of evaporation, a high temperature sintering is necessary to form the silicide. Argon is used as the sputtering gas which might be incorporated in the film. Though the high temperature sintering may remove most of the occluded gas, the film properties such stress can be affected by the residual gas in the film.[7]

4.1.3 Patterning

Silicides can be patterned by wet chemical etching, dry etching or lift-off techniques. Most silicides are soluble in HF containing solutions. If the substrate is not soluble in the etchant, a high selectivity can be obtained. However, the etching will be isotropic. leading to variations in the resistance values of the sensors. Dry etching is carried out in CF_4-O_2 and CCl_4-O_2 plasmas. Reactive ion etching (RIE) process is preferred in which the sputter etching of the metal components is enhanced by the reactive species such as F and Cl.[8-10] RIE produces anisotropic etching without undercutting and linewidth loss, so that sensors can be routinely produced with uniform resistance values. Another method to avoid the complications of etching is to use a lift-off process for delineating the patterns in silicides. A soluble mask such as a photoresist is first produced on the substrate and then the silicide film is deposited. Subsequently, the mask is removed by dissolving in a solution leaving the silicide pattern intact.

4.2 Silicon Carbide

SiC film is generally prepared by a high temperature CVD process.[11] Gases containing Si and C are used as the sources which are made to react at 900 to 1400 $^{\circ}$C. The Si containing gases generally used are SiH_4, Si_2H_6 and $SiCl_4$ and the carbon containing gases are CH_4, C_2H_4 and C_3H_8. The deposited film may be single or polycrystalline depending on the substrates used. On substrates like Al_2O_3 and quartz, polycrystalline films can be deposited at lower temperatures.

Reactive ion etching used to pattern SiC films. RF plasmas containing halogen gases are reacted with SiC to produce volatile products of Si and C. Standard photolithography techniques are used to generate patterns in photoresists. A secondary mask of SiO_2 is often used.

4.3 Diamond

Diamond film is also prepared by CVD processes. A gaseous source of carbon such as CH_4 is decomposed using a plasma, hot filament or thermal processes.[12,13] In presence of excess H or F, the following reactions take place.

$$CH_4 + H_2 \rightarrow C + 3H_2$$

$$CH_4 + 2F_2 \rightarrow C + 4HF$$
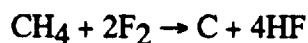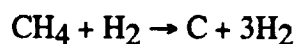
The carbon is deposited on the substrate in the form of graphite and diamond at an appropriate temperature is etched simultaneously by excess atomic hydrogen and fluorine in the following reaction:

$$C + 4H \rightarrow CH_4$$

$$C + 4F \rightarrow CF_4$$
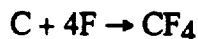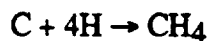
For a given temperature, the etch rate of graphite is considerably higher than the diamond etch rate; hence diamond will be deposited on the substrate. Using the halogen assisted process can produce diamond film on substrates maintained at 200 $^{\circ}$C.

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Patterning of diamond film is carried out by reactive sputtering etching in oxygen or fluorine. A secondary mask such as SiO_2 is patterned on the diamond film using standard photolithography and chemical or dry etching. The SiO_2 mask is durable in an oxygen or fluorine plasma. A selective growth of diamond film can be carried out on a substrate covered with SiO_2 masks or a pre-treated substrate.[14,15]

5. Conclusions

Requirements of material parameters of high temperature flow sensors are identified. Refractory metal silicides offer high temperature sensitivity and high frequency response and are stable up to 1000 °C. Intrinsic semiconductors of high bandgap are also considered as sensor elements. SiC and diamond are ideal materials. Combined with substrates of low thermal and electrical conductivity, such as quartz and Al_2O_3, these materials meet several requirements of high sensitivity and frequency response. Film deposition and patterning techniques suitable for these materials have been identified.

6. References

1.   C. B. Johnson, D. L. Carraway, P. Hopson, Jr, and S. Q. Tran, Proc. ICAF '87 Record, p.141-155.

2.   R. J. Vidal, WADC Tech Note 56-315, AD-97238, (1956).

3.   H. H. Lowell and N. Patton, NACA TN 3514, (1955).

4.   S. Albin, W. P. Winfree and B. S. Crews, J. Electrochem. Soc. Vol. 137 No. 6 (1990) 1973.

5.   L. I. Maissel and R. Glang, "Handbook of Thin Film Technology", Chapter 6, McGraw-Hill, 1970.

6.   S. M. Sze, "VLSI Technology", Second Edition, McGraw-Hill, 1988.

7.   S. P. Murarka, Thin Solid Films, Vol. 23, (1974) 323.

8.   T. Mochizuki, et.al., IEEE J. Solid State Circuits SC-15,(1980) 496.

9.   D. B. Fraser, et. al., J. Vac. Sci. Technol. Vol. 18, (1981) 345.

10.   S. P. Murarka, et.al., IEEE J. Solid State Circuits SC-15,(1980) 474.

11.   M. I. Chaudry and R. L. Wrght, J. Mater. Sci. Vol. 5 (1990) 1595.

12.   A. Feldman and S. Holy, eds. 'Diamond Optics', Proc. SPIE Vol. 969, 1988.

13.   A. Feldman and S. Holy, eds. 'Diamond Optics II', Proc. SPIE Vol. 1146, 1989.

14.   K. Kobashi, et. al., Proc. First Int. Symp. on Diamond and Diamond-like Films,
      Electrochem. Soc. Vol. 89-12 (1989) 139.

15.   J. S. Ma, et. al., Proc. First Int. Symp. on Diamond and Diamond-like Films,
      Electrochem. Soc. Vol. 89-12 (1989) 149.

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