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IMPREGNATION THERMODYNAMICS OF BARRIER-LAYER CAPACITORS

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ABSTRACT

Thermal analysis was applied to study the impregnation of barrier-layer capacitors On-stage impregnation was attempted The drastic weight loss above 900 ° C was attributed to bismuth release A thermodynamic analysis was undertaken to evaluate the situation It has been established that bismuth release is thermodynamically a distinct possibility in the constituent systems, $B-B_2O_3$, $Bi-Bi_2O_3$ and Pb–PbO, under the experimental conditions used in this study

INTRODUCTION

Ceramic barrier-layer capacitors (CBC) [1] consist of a thin insulating layer formed at the surface or at the grain boundaries of a piece of semiconducting ceramic In this case, a dielectric thickness of a few microns can be easily obtained in or on a piece of ceramic with a physical thickness of a few hundred microns The insulating layers are produced at the surface by surface re-oxidation, or at the grain boundaries by grain boundary re-oxidation or by impregnation of a second phase internally (called boundary-layer capacitors), depending on the type of CBC required Although initial interest was shown in $BaTiO_3$-based CBC [2], $SrTiO_3$-based CBC [3–5] became important later

Wernicke [6,7] proposed a two-layer model explaining the properties of $SrTiO_3$ boundary-layer capacitors He elaborated the formation of second-phase layers, incorporated the weight change into a quantitative equation and correlated it with the dielectric constant The relative weight change ($\Delta m/m \sim 3\%$) was determined by weighing the specimen before and after

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second firing, that is, impregnation This paper is a preliminary attempt to apply thermal analysis to study the impregnation The observations are explained on the basis of thermodynamic analysis

EXPERIMENTAL

Semiconducting $SrTiO_3$ was prepared by sintering 0.3 atm% Nb_2O_5-doped $SrTiO_3$ pellets in a reducing atmosphere (N_2, 75%, H_2, 25%) at 1350 °C The

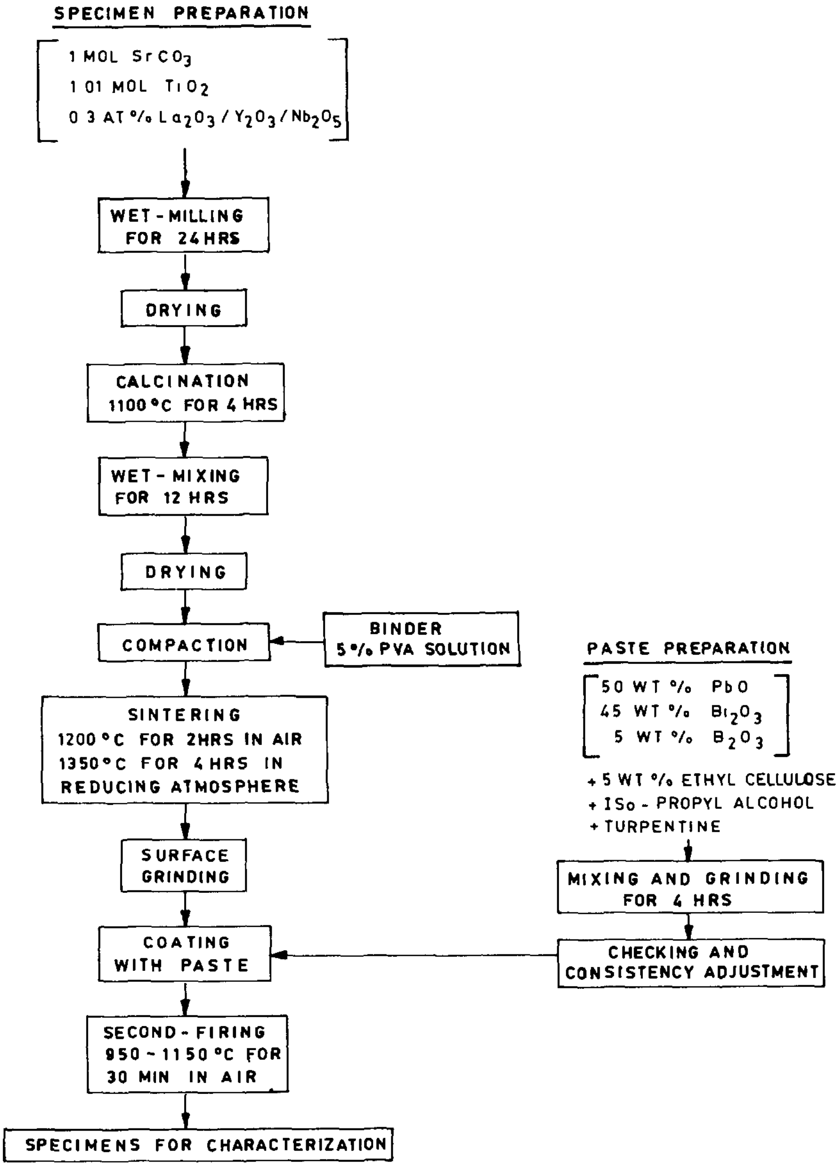

Fig 1 Flow chart for $SrTiO_3$ barrier-layer capacitors

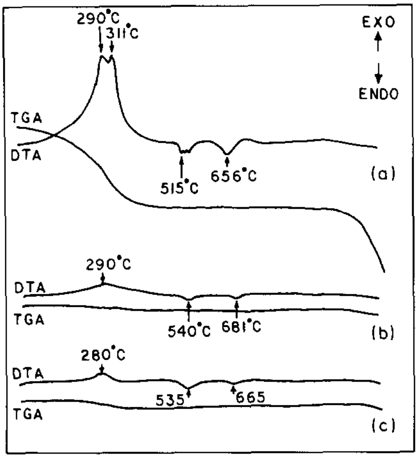

Fig 2 Thermograms of (a) dry oxide-paint powder, (b) well-mixed semiconducting $SrTiO_3$ and oxide-paint powders, (c) semiconducting $SrTiO_3$ pellet coated with oxide paint for on-stage impregnation

oxide paint prepared was applied to the surface of the semiconducting $SrTiO_3$ pellet and the second firing was carried out at 1000 °C for 30 min in air The flow chart of the whole process is shown in Fig 1 The dielectric constant of the prepared capacitor ranges from $1\ 0 \times 10^4$ to $1\ 5 \times 10^4$, while tan δ ranges from 0 06 at 10^6 Hz to 0 1 at 10^2 Hz with a minimum of 0 035 at 10^5 Hz [8] In this investigation, the dry oxide-paint powder, well-mixed $SrTiO_3$ and oxide-paint powders and the as-reduced $SrTiO_3$ pellet coated with oxide paint were thermally analysed (Stanton Redcroft, STA 780 Series) from room temperature to 1100 °C at a constant heating rate of 10 °C min^{-1} (see Fig 2) The semiconducting $SrTiO_3$ pellet was truncated to obtain a small cylinder which fitted into the DTA sample crucible Weighing was carried out before and after coating followed by drying On-stage impregnation was attempted on the coated pellet

THERMODYNAMIC ANALYSIS

The main constituents of the oxide paint are B_2O_3, Bi_2O_3 and PbO The thermodynamic stabilities of the oxide systems are required to understand and to obtain the desired reactions during impregnation and thus to obtain the necessary dielectric properties In this investigation, thermodynamic analysis was used to evaluate the situation

The three systems B–B_2O_3, Bi–Bi_2O_3 and Pb–PbO were considered Gibbs standard free energy values $\Delta G_T^{\ominus}$ were calculated from the reported

TABLE 1

Gibbs standard free energy of the reactions

$\Delta G_T^\ominus$ (cal) $= H_{(0)}^\ominus + aT\log T + bT^2 + cT^{-1} + IT$

T (K)	$H_{(0)}^\ominus$	$aT\log T$	bT^2	cT^{-1}	IT	$\Delta G_T^\ominus$ (cal)
$4/3\langle B\rangle + (O_2) = 2/3\langle B_2O_3\rangle$						
$\Delta G_T^\ominus = -201\ 383 + 10\ 10T\log T - 4\ 40\times 10^{-3}T^2 - 0\ 55\times 10^5 T^{-1} + 10\ 60T$ (298–723 K)						
373	−201 383	+9688	−612	−147	3954	−188 500
573	−201 383	+15962	−1445	−96	6074	−180 888
673	−201 383	+19223	−1993	−82	7134	−177 101
$4/3\langle B\rangle + (O_2) = 2/3\{B_2O_3\}$						
$\Delta G_T^\ominus = -209\,705 - 15\ 79T\log T + 1\ 42\times 10^{-3}T^2 - 1\ 67\times 10^5 T^{-1} + 92\ 12T$ (723–1800 K)						
773	−209 705	−35 252	+848	−216	+71 209	−173 116
973	−209 705	−45 908	+1344	−172	+89 633	−164 808
1173	−209 705	−56 849	+1954	−142	+108 057	−156 685
1373	−209 705	−68 024	+2677	−122	+126 481	−148 693
1573	−209 705	−79 399	+3514	−106	+144 905	−140 792
1773	−209 705	−90 949	+4464	−94	+163 329	−132 946

$\Delta G_T^\ominus$ (cal) $= A + BT\log T + CT$

T (K)	A	$BT\log T$	CT	$\Delta G_T^\ominus$ (cal)
$4/3\langle Bi\rangle + (O_2) = 2/3\langle Bi_2O_3\rangle$				
$\Delta G_T^\ominus = -91\,450 + 42\ 95T$ (298–544 K)				
373	−91 450	–	+16 020	−75 430
473	−91 450	–	+20 315	−71 135
$2/3\langle Bi_2O_3\rangle = 4/3\{Bi\} + (O_2)$				
$\Delta G_T^\ominus = -91\,926\ 67 + 42\ 29T$ (973–1093 K)				
773	−91 927	–	+32 690	−59 237
873	−91 927	–	+36 919	−55 008
973	−91 927	–	+41 148	−50 779
1073	−91 927	–	+45 377	−46 550
$2\langle Pb\rangle + (O_2) = 2\langle PbO\rangle$				
$\Delta G_T^\ominus = -105\,700 - 6\ 9T\log T + 68\ 86T$ (298–600 K)				
373	−105 700	−6619	+25 685	−86 634
573	−105 700	−10 905	+39 457	−77 148
$2\{Pb\} + (O_2) = 2\langle PbO\rangle$				
$\Delta G_T^\ominus = -105\,700 + 52\ 6T$ (600–760 K)				
673	−105 700	–	−35 400	−70 300
$2\{Pb\} + (O_2) = 2\langle PbO\rangle$				
$\Delta G_T^\ominus = -106\,600 + 51\ 4T$ (760–1150 K)				
773	−106 600	–	+39 732	−66 868
873	−106 600	–	+44 872	−61 728
973	−106 600	–	+50 012	−56 588
1073	−106 600	–	+55 152	−51 448

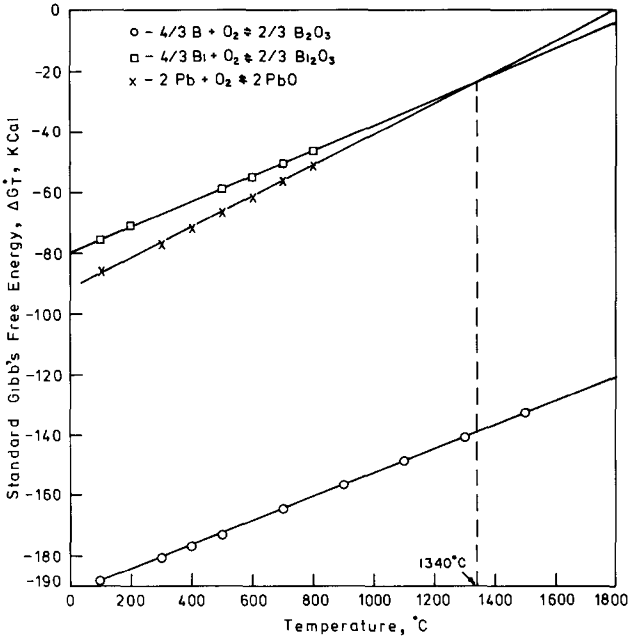

Fig 3 Standard Gibbs free energy vs temperature diagram for B_2O_3, Bi_2O_3 and PbO systems

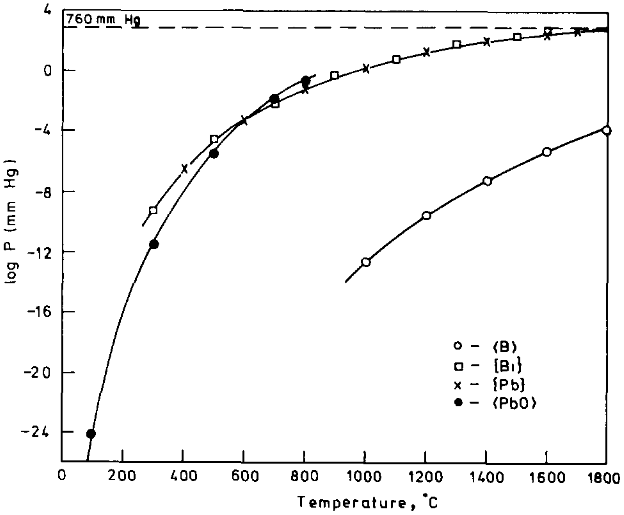

Fig 4 Temperature dependence of vapour pressure of ⟨B⟩, {Bi}, {Pb} and ⟨PbO⟩

TABLE 2

Vapour pressure of the species (log $P(\text{mmHg}) = AT^{-1} + B \log T + cT + D$)

T (K)	AT^{-1}	$B \log T$	CT	D	$\log P$	P
⟨B⟩						
$\log P = -29900T^{-1} - 1\ 0 \log T + 13\ 88$ (1000–2453 K)						
1273	−23 4878	−3 1048		+13 88	−12 7127	$1\ 9380\times10^{-13}$
1473	−20 2987	−3 1682		+13 88	−9 5869	$2\ 5888\times10^{-10}$
1673	−17 8721	−3 2235		+13 88	−7 2156	$6\ 0872\times10^{-8}$
1873	−15 9637	−3 2725		+13 88	−5 3562	$4\ 4032\times10^{-6}$
2073	−14 4235	−3 3166		+13 88	−3 8601	$1\ 3799\times10^{-4}$
2273	−13 1544	−3 3566		+13 88	−2 6310	$2\ 3386\times10^{-3}$
{Bi}						
$\log P = -10400T^{-1} - 1\ 26 \log T + 12\ 35$ (544 3–1953 K)						
573	−18 1501	−3 4753		+12 35	−9 2754	$5\ 3045\times10^{-10}$
773	−13 4541	−3 6391		+12 35	−4 7432	$1\ 8064\times10^{-5}$
973	−10 6886	−3 7650		+12 35	−2 1036	$7\ 8776\times10^{-3}$
1173	−8 8662	−3 8673		+12 35	−0 3835	0 4135
1373	−7 5747	−3 9535		+12 35	+0 8219	6 6356
1573	−6 6116	−4 0279		+12 35	+1 7106	51 3511
1773	−5 8658	−4 0934		+12 35	+2 3909	245 9590
1873	−5 5526	−4 1234		+12 35	+2 6740	472 0750
{Pb}						
$\log P = -10130T^{-1} - 0\ 985 \log T + 11\ 16$ (600–2013 K)						
673	−15 0520	−2 7856		+11 16	−6 6777	$2\ 1009\times10^{-7}$
873	−11 6037	−2 8969		+11 16	−3 3406	$4\ 5650\times10^{-4}$
1073	−9 4408	−2 9851		+11 16	−1 2660	$5\ 4205\times10^{-2}$
1273	−7 9576	−3 0583		+11 16	+0 1442	1 3937
1473	−6 8771	−3 1207		+11 16	+1 1622	14 5279
1673	−6 6550	−3 1751		+11 16	+1 9299	85 0867
1873	−5 4084	−3 2235		+11 16	+2 5281	337 3750
1973	−5 1343	−3 2457		+11 16	+2 7800	602 5370
⟨PbO⟩						
$\log P = -13480T^{-1} - 0\ 92 \log T + 0\ 35\times10^{-3}T + 14\ 36$ (298–1159 K)						
373	−36 1394	−2 3660	0 1306	+14 36	−24 0148	$9\ 6642\times10^{-25}$
573	−23 5253	−2 5375	0 2006	+14 36	−11 5023	$3\ 1459\times10^{-12}$
773	−17 4386	−2 6571	0 2706	+14 36	−5 4651	$3\ 4267\times10^{-6}$
973	−13 8541	−2 7491	0 3406	+14 36	−1 9026	0 01251
1073	−12 5629	−2 7882	0 3756	+14 36	−0 6155	0 2424

C_p values [9–12] or A, B and C values [13,14] and are given in Table 1 The temperature dependence of $\Delta G_T^{\ominus}$ for these systems is shown in Fig 3 The vapour pressures of ⟨B⟩ [15,16], {Bi} [17], {Pb} [18,19] and ⟨PbO⟩ [20] were calculated from the reported A, B, C and D values and are given in Table 2 Figure 4 shows the temperature dependence of log P The rate of

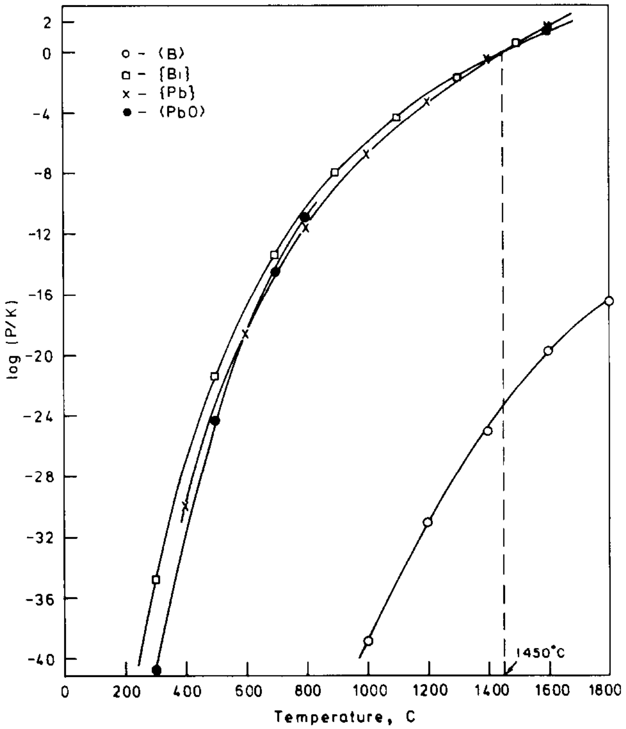

Fig 5 Temperature dependence of rate of volatilization ($V = P/K$)

volatilization $V = P/K$ was calculated for these species Figure 5 shows the temperature dependence of V

RESULTS AND DISCUSSION

Figure 2 shows the thermograms of the dry oxide-paint powder (a), well-mixed reduced $SrTiO_3$ powder and 5 wt% oxide-paint powder (b) and the reduced $SrTiO_3$ pellet coated with oxide-paint (for on-stage impregnation) (c) In Fig 2(a), there is a distinct overlapping of two exothermic peaks at 290 and 311°C and two endothermic peaks at 515 and 656°C The exothermic peaks associated with weight loss ($\Delta w/w = 13\ 55\%$) are a result of the burning off of organic matter, namely ethyl cellulose and turpentine A small part of the weight loss comes from the decomposition of H_3BO_3 to B_2O_3 The endothermic peaks without any weight loss are due to the melting of the mixture The striking feature is the drastic weight loss ($\Delta w/w = 26\ 62\%$) above 900°C which is attributed to the volatilization of one or more species of the oxide-paint In fact, this prompted the thermodynamic analysis

Both Figs 2(b) and 2(c) reveal similar features except that only one exothermic peak is observed It is important to note that there is no other chemical reaction The oxide-paint does not chemically react with the reduced $SrTiO_3$, either when it is well mixed with it in powder form, or when it is coated on the surface of the pellet Once again, the weight loss above 950 ° C is prominent An interesting point is the smooth increase in weight in the temperature range ~ 550–950 ° C before the drastic weight loss This is attributed to the impregnation process The weight gain during impregnation results essentially from two contributions (i) re-oxidation of reduced $SrTiO_3$ and (ii) diffusion of the insulating phase along the grain boundaries It is difficult to separate these two contributions The thermogram of on-stage impregnation (Fig 2(c)) clearly indicates the possibility of studying the process in detail With instrumentation of higher sensitivity and sophistication, a finer fingerprint of the process may be obtained which will facilitate the interpretation

Thermodynamically, B_2O_3 is the most stable of the three systems under consideration at any temperature in this study, i e up to 1800 ° C (see Fig 3) Bi_2O_3 and PbO are of similar stability Up to 1340 ° C, Bi_2O_3 is the least stable, whereas PbO is the least stable above 1340 ° C In the case of the temperature dependence of the vapour pressure, $\{Bi\}$ and $\{Pb\}$ are similar, whereas $\langle B \rangle$ has the lowest value, significant only above 1000 ° C (see Fig 4) Bi_2O_3 and PbO are equally volatile

The rate of volatilization V, the deciding factor for the present situation, is a function of the vapour pressure of a species at a certain temperature and the corresponding reduction constant of the reaction at that temperature In Fig 5, the volatilization rate of bismuth is ~ 4 orders of magnitude greater than that of lead at 400 ° C However, this is reduced to ~ 1 order of magnitude at 1000 ° C Above 1450 ° C, the volatilization rate of lead becomes more than that of bismuth and the difference increases with a further increase in temperature Boron, although significant only above 1000 ° C, has the lowest rate of volatilization throughout From Fig 5, it is obvious that bismuth is the first to be released in the process, closely followed by lead Within the temperature of interest, i e up to 1100 ° C, thermodynamically bismuth is the most volatile species Lead release is a thermodynamic possibility above 1450 ° C

The stability of the oxides of bismuth is a well-known problem The present thermal and thermodynamic analyses suggest an impregnation temperature of ~ 900–950 ° C If the impregnation is carried out above 950 ° C, tolerance must be provided for bismuth/lead release With progressive bismuth release the atmosphere of impregnation becomes continuously enriched with bismuth, which should also be considered

CONCLUSIONS

(i) Thermal analysis can be effectively applied to study the impregnation of barrier-layer capacitors

(ii) Thermodynamically, bismuth release is a distinct possibility during impregnation

(iii) The ideal impregnation temperature is ~ 900–950 ° C, although the diffusion coefficients and other parameters should also be taken into account

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