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EFFECT OF V_2O_5 DOPANT ON THE ELECTRICAL CONDUCTIVITY OF RuO_2 THICK FILM RESISTORS

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Thick film glaze resistors have been prepared using V_2O_5 doped RuO_2 conducting phase. Different amounts of V_2O_5 were incorporated into RuO_2 lattice by solid state reaction. Sheet resistivity decreased from 235 to 10 kΩ/Sq. with the increase in the dopant concentration from 2 to 6% wt. The conductivity, 'σ', was found to fit in the equation $\sigma = KS(1-S)$, where S is the probability that a given cationic site will contain an extra charge carrier and $K = 10^{-3}$ mho-sq.

INTRODUCTION

Thick film resistors are now mainly based on RuO_2 and CdO. The sheet resistivity (ρ_S) and the temperature coefficient of resistance (TCR) can be controlled by the so called 'Controlled Valency'.[5,10,13] In addition, the composition of the glass and its content[10] also determine these properties.

Solid solutions in which the dopant atoms have a valency different from that of the host atoms are classified into the following three categories, controlled atomic imperfections,[1,2] induced valency[3] and controlled valency.[4]

The present work is concerned with the third method. Atoms of the parent crystal may be made to change their valency as a result of the introduction of foreign atoms When Li^+ is introduced into the lattice of NiO, equivalent number of Ni atoms change their valency ($Ni^{2+} \rightarrow Ni^{3+}$) without the formation of atomic imperfections and maintain charge neutrality. This is termed as 'Controlled Valency'. The deviating valency of a metal oxide can be usefully controlled in this way, particularly so in the case of thermistors and resistors. The ionic radii of the host and dopant ions must also be compatible.

In the case of thick film resistors, dopants have been used to control the TCR and ρ_S. Effect of Li^+ and Sb^{5+} on PbO[11] and Sb^{5+} on In_2O_3[12] have been studied.

Iles[5] assumed that RuO_2 was partially deficient in oxygen and argued that it contained a corresponding amount of Ru^{3+}. With this premise, he used Nb_2O_5 which had all the requirements of a dopant with respect to matching of ionic radii and applicability of Vegard's law. His stress was more on the controlling of TCR. He used silver, additionally, to control ρ_S.

In order to get a wide range of resistivity values, it is of primary importance to study the effect of dopant concentration on ρ_S. RuO_2-based thick film resistors are now considered.

EXPERIMENTAL

Controlled Valency Process in RuO_2

We have used pentavalent vanadium as the dopant. V^{5+} has a smaller ionic radius of

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0.59 Å compared to 0.67 Å of Ru^{4+}, thus satisfying the primary condition. The incorporation of V^{5+} ion into the quadrivalent host lattice (RuO_2) is expected to lead to a mixed valence compound,

$$V_x^{5+}\, Ru_x^{3+}\, Ru_{(1-2x)}^{4+} O^{2-} \tag{1}$$

The excess oxygen is ejected out into the gas phase as $1/2O_2$ as a result of the incorporation of two vanadium ions. This leaves behind two electrons in the crystal which converts Ru^{4+} ions to Ru^{3+} ions. This type of substitution is similar to introducing La^{3+} into $BaTiO_3$ (replacing Ba). Here small amount of Ti^{4+} ions reduce to Ti^{3+} in order to maintain charge neutrality. This differs from that of Iles study.

Preparation of RuO_2-X V_2O_5 Composition

RuO_2(Fluka) and NH_4VO_3 (Reanal, Hungary) were reacted by taking the corresponding quantities. V_2O_5 varied from 2 to 6% wt. The mixtures were reacted at 1000°C for 24 hours in platinum crucibles.

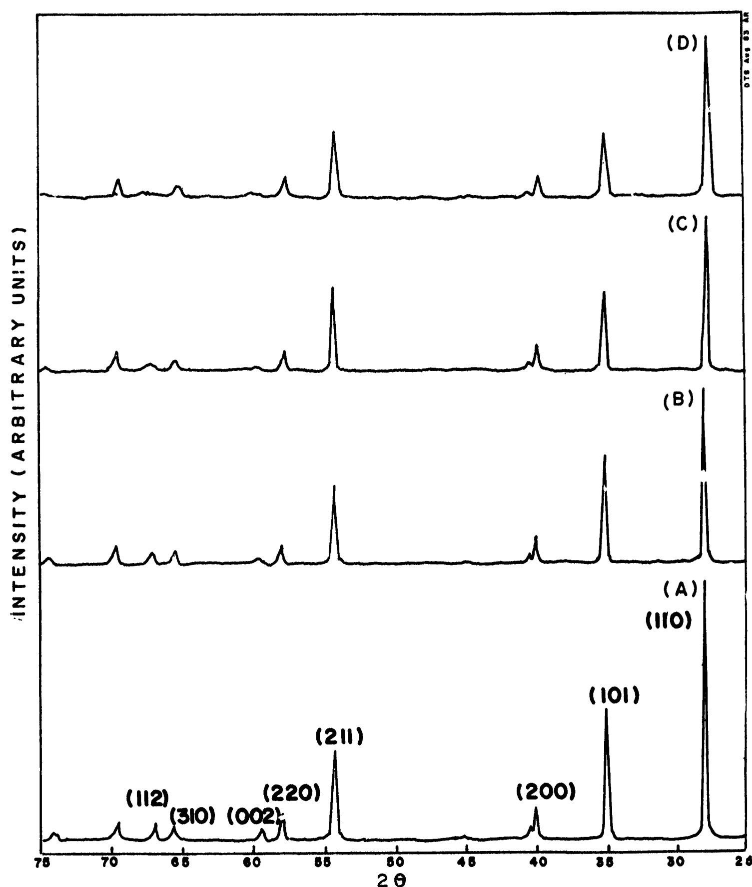

FIGURE 1 X-ray diffractograms of the RuO_2-XV_2O_5 compositions. (A) RuO_2, (B) RuO_2-2%V_2O_5, (C) RuO_2-4%V_2O_5 and (D) RuO_2-6%V_2O_5.

An X-ray diffractometer was used for X-ray analysis of the compositions. A Cu target was used for X-ray generation.

The system had tetragonal rutile structure. The lattice parameters were calculated on this basis. Figure 1 shows the diffractograms of RuO_2 and RuO_2–XV_2O_5 compositions. Variation of the lattice parameter values with the mole % of V_2O_5 is presented in Figure 2. Traces of V_2O_5 were present in the compositions where the dopant was greater than 6%. Lattice parameter 'c' decreases and 'a' increases with the increase in the V_2O_5 concentration. It is clear from this figure that the RuO_2–XV_2O_5 system obeys Vegard's law. The lattice parameters of RuO_2 (host oxide) vary linearly with the dopant concentration (V_2O_5). The increasing order in the 'a' value is due to the increase in the presence of Ru^{3+} which has greater value of ionic radius (0.74 Å) compared to 0.59 Å of V^{5+} and 0.67 Å of Ru^{4+}.

Paste Formulations

The resistor pastes formulations were made using RuO_2, RuO_2–XV_2O_5 as electroactive materials and a lead-borosilicate glass in the ratio 30:70. The vehicle consisted of 8% ethyl cellulose in a solvent mixture consisting of butyl cellosolve, terpineol and butyl

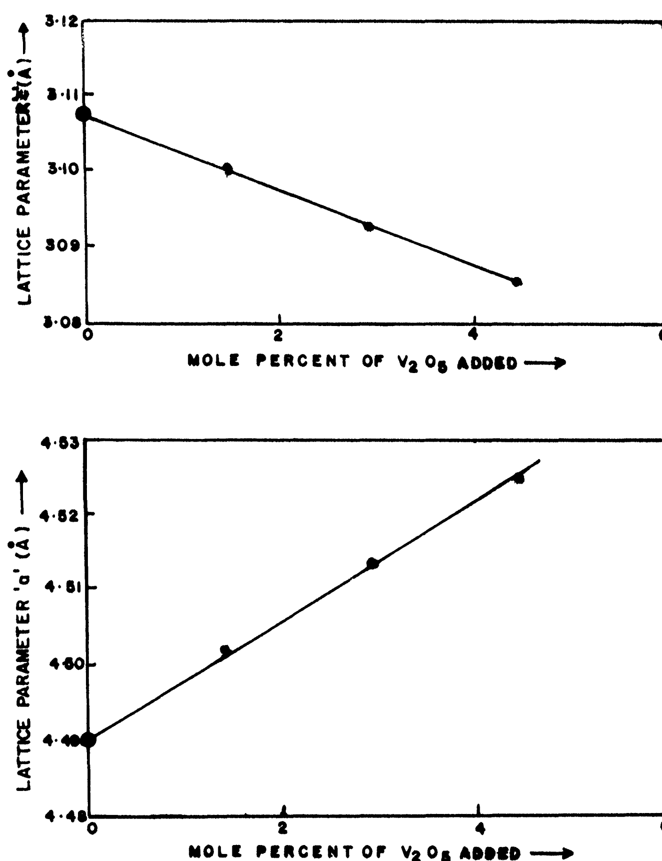

FIGURE 2 Effect of addition of V_2O_5 on lattice parameters of RuO_2.

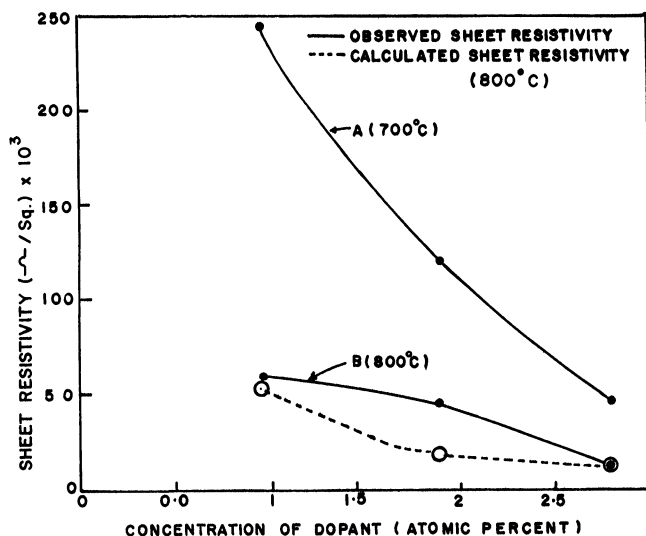

FIGURE 3 Variation of sheet resistivity (ρ_S) with dopant concentration.

carbitol acetate. The thick films were deposited on 96% Alumina substrates by screen printing the paste formulations using stencils (200 mesh, size: 2 mm.× 10 mm.). The films were dried (150°C/10 min. under IR lamp) and fired in a thick film furnace at various peak firing temperatures. Silver terminations were used for the electrodes.

RESULTS AND DISCUSSIONS

Variation of Sheet Resistivity (ρ_S) with Dopant Concentration

The data is presented in Figure 3. The ρ_S decreases with the increase in the dopant concentration for the resistors fired at 700°C and 800°C. The decrease for 'A' is steeper from 235 to 46 kΩ/square compared to that of 'B' which is 60 to 11 kΩ/square. The lower values for 'B' are because of sintering effects. The particle nodules fuse to form bigger agglomerates. Moreover, the glass becomes thinner and flows down to the substrate surface at higher temperatures. These effects are found to be common for all dopant concentrations. The effect of the increase in the dopant content, however, is reflected in the decrease in ρ_S. The increase in the conductivity is attributed to the loss of oxygen. Consequent to the incorporation of V_2O_5 into RuO_2, the electrons left behind created Ru^{3+} species. The (+3) charge is not localized and is free to move from one Ru site to another. And this results in the increase in electrical conductivity.

Sheet Resistivity of undoped RuO_2 Thick Film Resistors

The stoichiometry of RuO_2 (starting material) was indirectly confirmed. The lattice parameters obtained for the compositions with different dopant concentrations were plotted. The graph was extrapolated to zero dopant concentration condition following the practice.[6] Figure 2 represented this situation. The extrapolated lattice parameter values for zero dopant concentration corresponded to those observed for RuO_2.

It has been reported that non-stoichiometric (oxygen deficient) RuO_2 was obtained by heating stoichiometric RuO_2[7] or by the incomplete oxidation of Ru.[8] In either case,

equivalent number of Ru atoms assumed lower valence state and released electrons for conduction following the equation,

$$Ru^{4+}O_2^{2-} \rightarrow Ru^{4+}_{(1-2x)}Ru^{3+}_{2x}O^{2-}_{(2-x)} + 2X(e) \qquad (2)$$

It is, therefore, interesting to note when undoped RuO_2-based thick film resistors are fired, one will expect them to be partially deficient in oxygen with corresponding amounts of Ru^{3+} present. Considering 4.9% of oxygen loss, the sheet resistivity of thick film resistors is computed to be 7.4 kΩ/square. This is in broad agreement with the observed value of 9.52 kΩ/square taking into consideration the effect of glass composition and firing temperature etc.

Computation of Sheet Resistivity Values

Following Honig,[9] the conductivity, σ can be given by

$$\sigma = KS(1-S) \qquad (3)$$

where σ = electrical conductivity, S = probability that a given cationic site will contain an extra charge carrier.

Honig considered M^n and $M^{(n+1)}$ cations in different valence states of n^+ *and* $(n+1)^+$ respectively. He then showed that

$$S = \frac{M^n}{M^n + M^{n+1}} \qquad (4)$$

In our case, $M^n = Ru^{3+}$ and $M^{(n+1)} = Ru^{4+}$. The concentration of Ru^{3+} ions was taken as equal to V^{5+} ions.[1] Using the equations (3) and (4), the resistivity values of thick film resistors of the system RuO_2-$X_2V_2O_5$ were calculated. 'S' values were also calculated corresponding to 2,4 and 6% wt of V_2O_5 in the compositions. It was found that our resistivity values fitted well in the equation (3) when $K = 10^{-3}$. The units of 'K' turned out to be mho-sq. according to dimensional analysis, since 'S' was the ratio of numerical values. All the data are presented in Table I.

The value of 'K' depends on

1) Glass composition.
2) Ratio of glass to the mixed oxide system.
3) Firing temperature.
4) Aspect ratio of the resistor print.

From the above table, it is seen that the calculated and measured sheet resistivity values match well.

CONCLUSIONS

V_2O_5 could successfully be inducted into RuO_2 lattice to about 6% by solid state reaction forming mixed valence oxide system like V^{5+} $Ru^{3+}Ru^{4+}_{(1-2x)}O^{2-}$. X-ray results confirmed that the incorporation of the dopant followed Vegard's law.

Thick film resistors were prepared using the above mixed valence oxide compositions, a leadborosilicate glass and fired at 700°, 800 and 900°C peak firing temperatures.

TABLE I
Sheet resistivity data with respect to the dopant concentration

Sr. No.	Wt% of V_2O_5	At% of V^{5+}	At% of Ru^{4+}	$S = \frac{V^{5+}}{V^{5+} + Ru^{4+}}$	Calculated ρ_s kΩ/sq.	Measured ρ_s 700°C	kΩ/sq. 800°C	900°C
1.	2	0.962	32.214	0.0290	35.53	235.37	60.03	33.24
2.	4	1.899	31.120	0.0575	18.46	119.15	43.43	17.31
3.	6	2.807	30.058	0.0854	12.80	46.05	11.35	10.52

Keeping the glass composition, the ratio of the mixed valence oxide to the glass and the peak firing temperature constant, the ρ_S values varied with the dopant concentration. Computed ρ_S values had a broad agreement with the observed ones for RuO_2-based thick film resistors.

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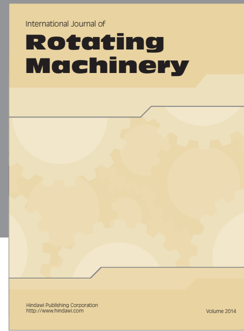
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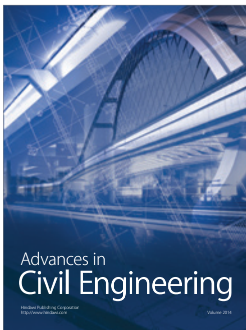
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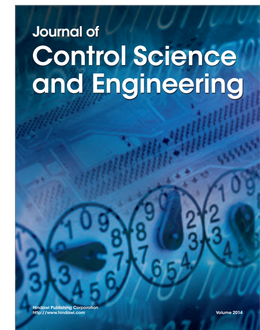
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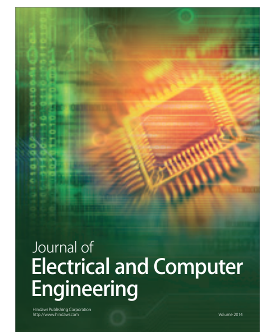
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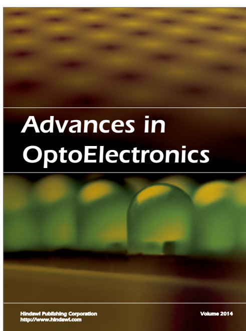
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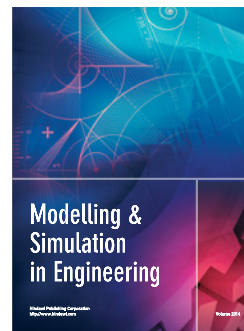
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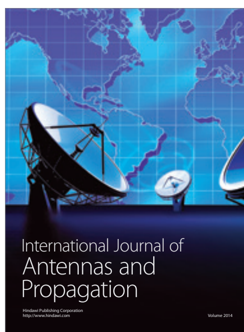
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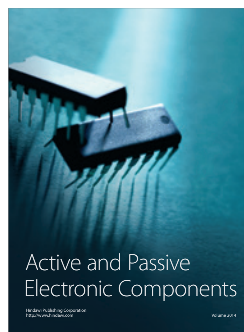
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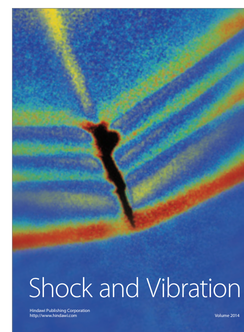
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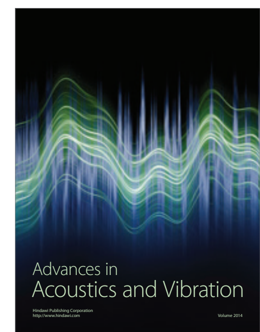
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