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MEMS BASED NANOCRYSTALLINE METAL OXIDE GAS SENSORS FOR COALMINE ENVIRONMENT

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ABSTRACT

Conventional Metal Oxide gas sensors commonly used for sensing inflammable hydrocarbon gases and other toxic gases suffer from the two limitations, viz. (a) their relatively high operating temperature (≥300° c) and (b) large power dissipation (≥1 Watt). In this paper we establish that use of nanocrystalline metal oxide in place of polycrystalline metal oxide lead to large increase of free surface energy which in turn leads to lower adsorption isotherm and large surface concentration and hence enhances reaction rate even at a much lower temperature. Moreover a simple software tool has been developed to analyze the heat dissipation (power consumption) components and to design optimum microheater for a particular operation.

1.INTRODUCTION

Conventional sensors used either electrochemical types having very short life for continuous operations or Figaro types (metal oxide on alumina substrate), which consumes large power (~1 Watt) and needs high operating temperature (~300° c) and long response time. Both these types are unacceptable for continuous gas monitoring in underground coalmines for which considerable improvement in the design and characterization of metal oxide gas sensors are essential [1-5]. The present work is motivated to solve these problems by taking a twin approach of (a) reducing the operating temperature through the use of proper nanostructures of metal oxide (theoretically the variation of reaction rates with dimension for various nanostructures eg. Nanobelts ,nanocubes, nanotubes etc. has been calculated) . (b) reducing the power dissipation through the deployment of MEMS structure (properly designed microheater) with thin membrane for active layer deposition.

2. ESTIMATION FOR VARIATION OF REACTION RATE WITH DIMENSION

Rate of reaction on a surface will depend on rate of adsorption on the surface to some extent .On surface of any dimension, the rate of adsorption is mainly governed by a) The rate of arrival of molecules at the surface b) The proportion of incident molecules which undergo adsorption
i.e. we can express the rate of adsorption R(per unit area of surface) as $R_{ads}=S.F$

$$R_{ads}= \{f(\theta).P.\exp(-E_a/RT)\}/(2\Pi mkT)^{1/2}$$

where, once again, E_a is the activation energy for adsorption and $f(\theta)$ is some, as yet undetermined, function of the existing surface coverage of adsorbed species which depend upon the types of isotherm. (for the Langmuir isotherm $f(\theta) = (1-\theta)$,P - gas pressure, m - mass of one molecule, T - temperature .[1]

The most important factor which mainly determines the rate of adsorption (and hence rate of reaction) is the change in free energy of the surface. The total surface free energy can be divided in mainly two parts $\Delta E_{free}=\Delta E_{Surface}+\Delta E_{Edge}$

Where $E_{Surface}$ and E_{Edge} are proportional to the surface area($=K_1A$) and length of the edge($=K_2L$) ,K_1 and K_2 being the rate constant.

The effective activation energy is thus given by $E=E_a+\Delta E_{free}$ leading to the final expression of S as $S=f(\theta).\exp(-E_a/RT)\exp(\Delta E_{free}/RT)$,

and R_{ads} as $R_{ads}=\{f(\theta).P.\exp(-E_a/RT)\exp(\Delta E_{free}/RT)\}/(2\Pi mkT)^{1/2}$

If we keep the activation energy, temperature and pressure constant and measure the adsorption rates for different surfaces at the same surface coverage for different structures of nano-crystalline material then adsorption rates only depend on the change in ΔE_{free} .

Thus $R_{ads}=K.\exp(E_{surface}/RT)\exp(E_{edge}/RT)=K\exp(K_1.A)\exp(K_2.L)$

Since conc. of adsorbent molecules remains constant, we should have

Reaction Rate= K_2. [conc. of adsorbed species]= K_2. R_{ads}. t

In nano-crystalline material the exposed surface area and the edge lengths become larger compared to bulk material . Thus extra energy term plays an important role in determining reaction rate on the nano-crystalalline surface.

But different nano structures has different surface to volume ratio (SVR) and different edge to volume ratio (EVR) .So if we consider a fixed volume of different nano structure (say unit volume) then A = SVR and L = EVR.Table 1 and 2 represents the SVR and EVR of various geometrical forms of nanostructures and their dimension.

Table 1 : SVR and EVR for different structures

Structure	SVR	EVR	Parameter Spcification
Cubic	$\frac{6l^2 + ld/2}{(l+d/2)^3}$	$\frac{12l + d}{(l+d/2)^3}$	l =length of side of cube d=separation of 2 cubes
Hemispherical	$\frac{1}{r} + \frac{r}{(r+d/2)^2}$		r=radius d=separation
Tubes	$\frac{2(a+b)}{(b+d/2)^2} + \frac{1}{h}$	$\frac{2(a+b)}{h(b+d/2)^2}$	a=inner diameter b=outer diameter h=height d=separation
Belts	$\frac{2l}{(l+d/2)^2} + \frac{1}{h}$	$\frac{2l}{h(l+d/2)^2}$	l=length of belt h=height d=separation

Table 2 : SVR and EVR in terms of dimensions

Structure	Specification	SVR	EVR
Cubic	l = d = x	1.9259/x	$3.8519/x^2$
Hemispherical	r = d = x	2.106/x	0
Tube	a/4=b/6=h/10 = d/6 = x	2.7/x	$1.727/x^2$
Belt	l/10 = h/100 = d = x	.98/x	$0.03004/x^2$

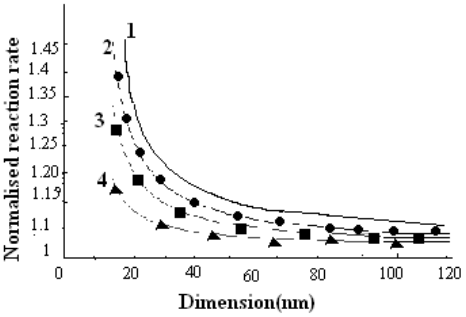

Fig1. Reaction rates (normalized) for different nano structures at different dimensions

(1=tube 2=hemisphere3=cube 4= belt)

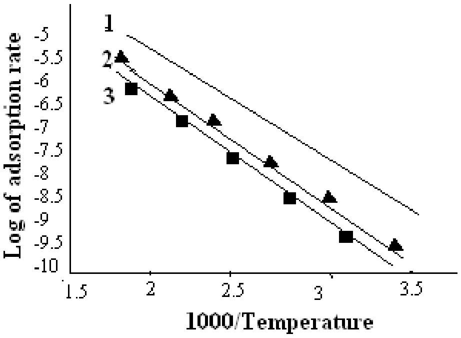

Fig.2. Rate of reaction for different dimension at different temperature

(1=1-10 nm 2=10--100nm 3=>1000nm)

Fig.1. displays the variation of normalized reaction rate of different nanostructures and Fig.2. shows how the variation of adsorption rate with temperature. One observes that as the dimensions reduce below 20 nm or so , the reaction rate increases significantly leading to lowering of reaction temperature correspondingly. It is further observed that nanotube structure lead to higher adsorption rate as compared to other types of nanostructures.Thus , for achieving lowest reaction temperature , nanotubes having dimensions less than 20-30 nm are the most preferred nanostructures for most cases.

4. THERMAL DESIGN

Another important thermal consideration of gas sensors in underground coalmines is the design of microheaters which will consume very low power from the battery supply of the signal processing unit for the gas sensors embedded in the coalmines.Fig.3. shows the side view of the MEMS metal oxide gas sensor with embedded microheater and Fig.4. shows the different pathways of heat transfer from the MEMS structures. Different heat loss components (ie.power consumption for achieving a particular temperature) Qa,Qb,Qc and Q_{total} have been calculated after detail theoretical calculation[6]. For membrane dimension $5X5mm^2$ different components are as shown Qa=0.615W,Qb=0.5239W,Qc=0.0689W and Q_{total}=Qa+Qb+Qc=1.2078.However with reduction in the membrane dimension (1mmX1mm) there is significant reduction in power consumption (Q_{total}=Qa+Qb+Qc=41+34.92+4.59=80.46mW) which is also supported by softwares like Coventorware.[6]

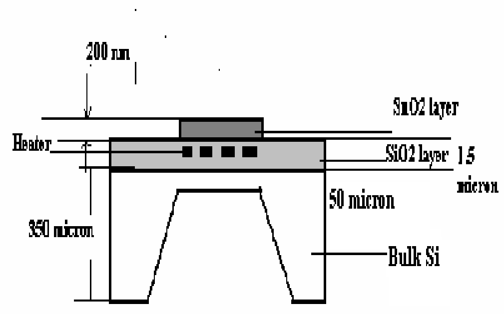

Fig.3: Side view of the MEMS metal oxide gas sensor

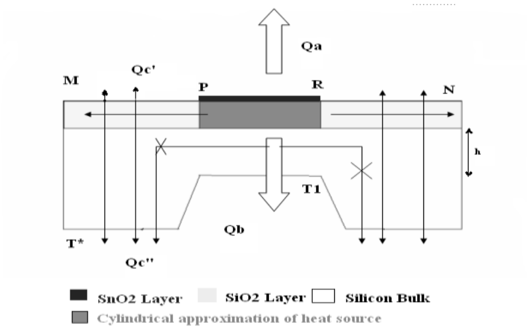

Fig. 4: Pathways of heat flow

5. CONCLUSIONS

A phenomenological analysis for estimating the variation of reaction rate of metal oxide gas sensors with the variation of its nanocrystalline structure has also been carried out with a view to identify its most suitable nanocrystalline structure for gas sensing at lowest possible temperature . It is found that for achieving lowest reaction temperature , nanotubes having dimensions less than 20-30 nm are the most preferred nanostructures for gas sensing .

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