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Hydrothermal synthesis of TiO_2 using $TiCl_3$ with Nutrients and gas sensing performance of TiO_2 thick films

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Abstract: In this work TiO_2nanoparticals of hexagonal shape were prepared by using $TiCl_3$, the TiO_2 thick films were prepared by using screen printing technique. The films were characterized by scanning electron microscopy (SEM), UV visible technique, Transmission electron microscope (TEM) and Selected area diffractogram (SAED). The effect of change in nutrient such as water, NH_4 and seed of nano TiO_2 on the structural, morphological and gas sensing properties of the films were studied and discussed. Thick films of Hydrothermal synthesized TiO_2 using $TiCl_3$ and water is sensitive to LPG, When NH_4 is used as nutrient thick film were sensitive to H_2 gas and for TiO_2 nano seed it is sensitive to H_2S gas.

Keywords: Hydrothermal synthesis, TiO_2 nanoparticles, thick films, sensors.

Introduction

In past decades the titanium oxide is one of the most studied oxides for different application such as pigments, solar cell[1],biomaterials[2],photocatatalysts[3],photovoltaics[4],electrochromic windows and displays[5-8] and sensing applications [9-12]. The different methods can be used to synthesis TiO_2 nanorods, nanotubes, nanoparticals and microspheres such as sol-gel method, Micelle and inverse micelle methods, sol method, solvothermal method, direct oxidation method, chemical vapor deposition, physical vapor deposition, electrode position, sonochemical, method, microwave method and hydrothermal method. There are several ways of preparing TiO_2 particles [13-16]. The hydrothermal method has many advantages like producing a highly homogeneous crystalline product, which can be obtained directly at relatively lower reaction temperature. Its most important feature is that decrease in agglomeration between particles, Phase homogeneity and controlled particle morphology. It also offers the uniform composition, purity of product, mono dispersed particles and control over the shape and size of the particles. In recent years, heterocontact between p and n-type semiconducting grains have been developed for detecting varies gases [17-20].These semiconducting gas sensors possess a gas sensing mechanism different from single oxide semiconductors, and can detect small amount of toxic gases that exist in air. The most general gas sensing mechanism [12–17] of semiconductor gas sensors proposed is a simple resistivity change due to adsorption–desorption of gases. The p–n heterocontact concept was used in the present investigation [21–30].There is an intrinsic difference in the behavior between the heterocontact type sensors and the sensors based on catalytic oxidation/reduction of gas molecules. The heterocontact type sensors work on the principle of barrier mechanism, which needs no adsorption and desorption of oxygen for the detection gas from air.
In this work TiO_2 nanoparticals of hexagonal shape were prepared by using $TiCl_3$, the TiO_2 thick films were prepared by using screen printing technique and its gas sensing properties were investigated.

Experimental

A. TiO_2 powder preparation

To prepare TiO_2 powder, $TiCl_3$ were usedas a source material. 20 ml of $TiCl_3$ wasadded in 2 ml dil HCl. NH_3 was drop wise added in solution.The solution was filtered and precipitate was dried for 3h.

B. Hydrothermal synthesis of TiO_2

The TiO_2nano particles of rice grain shape were synthesized by a hydrothermal method.To prepare sample-A, 1 gm of TiO_2 powder was added in160 ml water. Thesolution was stirred at room temperature for 20 min. The mixture was put into a Teflon-lined stainless autoclave which was heated at 180^{o}C for 12h. For sample-B, 1 g of TiO_2 powder was added in 160 ml of liquid ammonia. Solutions were stirred at room temperature for 20 min. The mixture was put into a Teflon-

lined stainless autoclave which was heated at 180°C for 12h. For sample-C, mixing of 0.5 g of TiO_2 powder was 0.5 g TiO_2 seed (commercially prepared TiO_2nano particles of size <25 nm) wereadded in 160 ml water. Solution was stirred at room temperature for 20 min. The mixture was put into a Teflon-lined stainless autoclave which was heated at 180°C for 12h.After heat treatment the sample A, B and C were naturally cooled to room temperature. The white precipitate was washed by de-ionized water and dried at 100°C for 2 h.

C. Preparation of TiO_2 thick film

The thixotropic paste was formulated by mixing the fine powder of Sample A (nano TiO_2) with the solution of ethyl cellulose (a temporary binder) in a mixture of organic solvent The paste was screen printed on the glass substrate in the desired pattern. The film was fired at 550°C.for 30 min. silver contact was made for the electrical measurements. Similarly thick films using sample B and C were prepared.

D. Thickness measurements

The thickness of the films was observed in the range from 25 to 30μm. The reproducibility in thickness of the films was possible by maintaining the proper rheology and thixotropy of the paste.

E. Details of gas sensing system

The sensing performance of the thick film sensors was examined using a 'static gas sensing system'. A heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and the current was measured by a digital picoammeter. Air was allowed to pass into the glass chamber after every gas exposure cycle.

Result and Discussion

A. UV- visible spectra of synthesized TiO_2

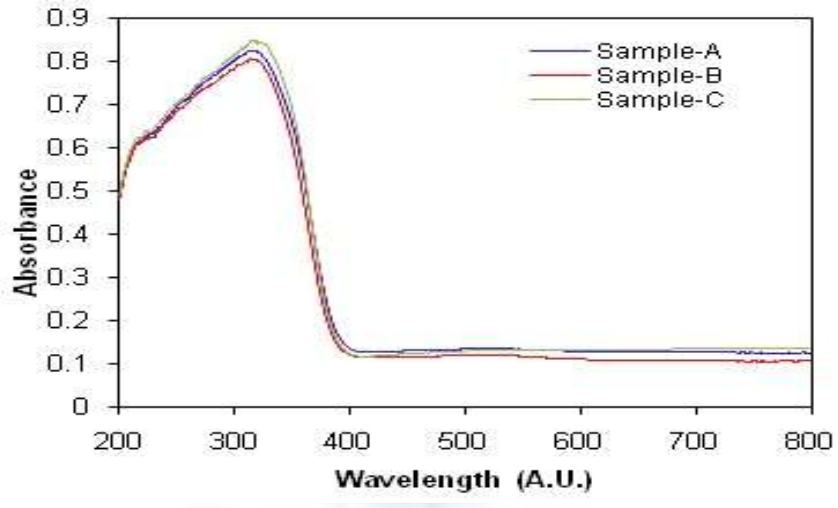

Fig. 1. U-V visible spectra of sample A, B and C.

Fig.1 shows the UV-visible spectra of hydrothermaly synthesized TiO2 powder.This spectra of TiO2 is in the wavelength range of 200-800A.U.The maximum absorbance is 0.83 for wavelength 332A.U. and band gap is 3.73eV, for sample A, B and C. The TiO_2 exists in three different crystals modifications, that is as anatase (tetragonal crystal structure with 3.2eV energy gap [13]), rutile (tetragonal crystal structure with 3.2eV energy gap), and brookite (orthorhombic with 2.96eV energy gap). Among the three phases rutile is most stable phase, which can be hydrothermally prepared.

B. X-Ray diffraction analysis

Fig.2 depicts an XRD pattern of TiO_2 powder (Sample A, B and C). X-ray diffraction analysis of this powder was carried out in the 20-80 deg. (2θ) range using Cu-Kα (with λ= 1.54Å, 40 kV, 30mA) radiation. The observed peaks matched well with the reported PDF 01-070-2556[31] data confirming the polycrystalline nature. The higher peak intensities of an XRD pattern are due to the better crystalline nature. The percentage crystanillity is 92.2%, 93.1%, 93.4% and grain size were estimated to be 2.77nm, 2.62nm and 2.95nm using Scherrer formula for Sample A, B and C respectively.

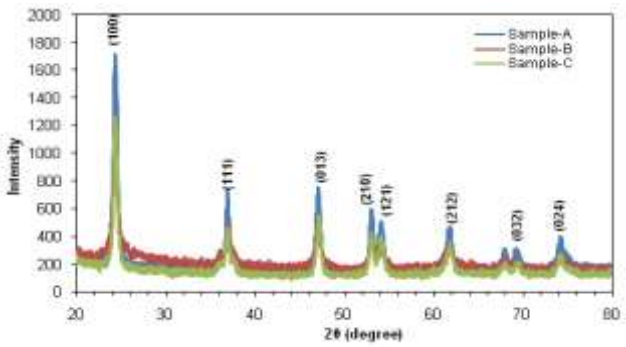

Fig. 2. X-Ray diffraction pattern of sample A, B and C.

C. Electrical conductivity of TiO_2 thick films

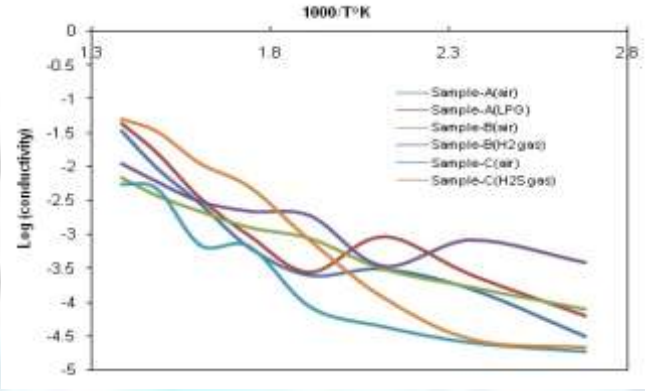

Fig.3. Variation of conductivity with temperature for TiO_2 thick films.

Fig.3 represents the variation of conductivity with temperature for thick films. It is clear from the graphs that the conductivity is varying approximately linearly with temperature. Conductivity of the films goes on increasing with an increase in temperature. Hence resistivity goes on decreasing with increase of temperature. Therefore, material exhibit negative temperature coefficient of resistance (NTC).

D. Microstructures analysis by SEM

The micro structural and chemical compositions of the films were analyzed using a scanning electron microscope (SEM, JEOL JED 6300) coupled with an energy dispersive spectrometer (EDS,JEOLJED2300LA). Fig. 4 (a, b and c)depicts a SEM image of TiO_2 thick film fired at 550^o C(sample A,B and C). The films consist of voids and a wide range of particles distributed uniformly.

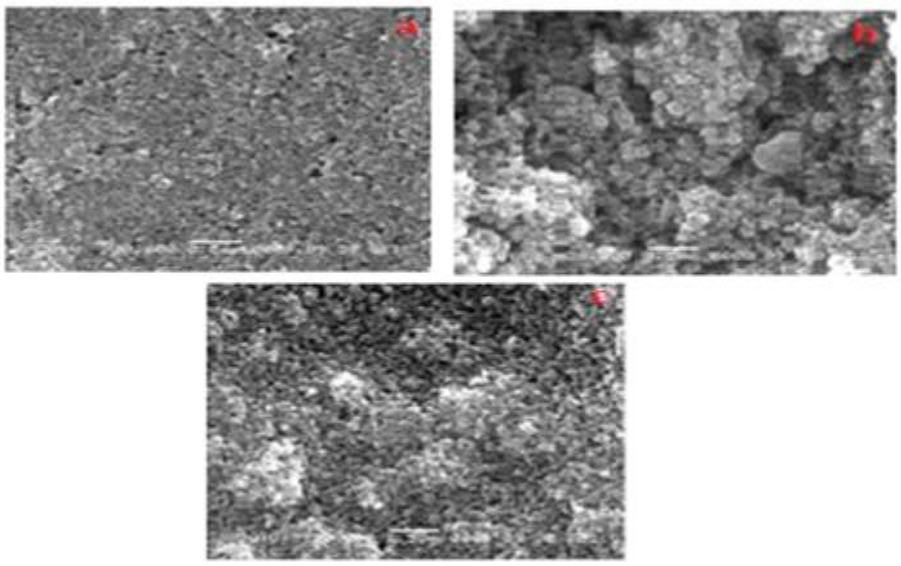

Fig. 4(a, b, c). SEM images of TiO_2 thick films.

E. TEM analysis

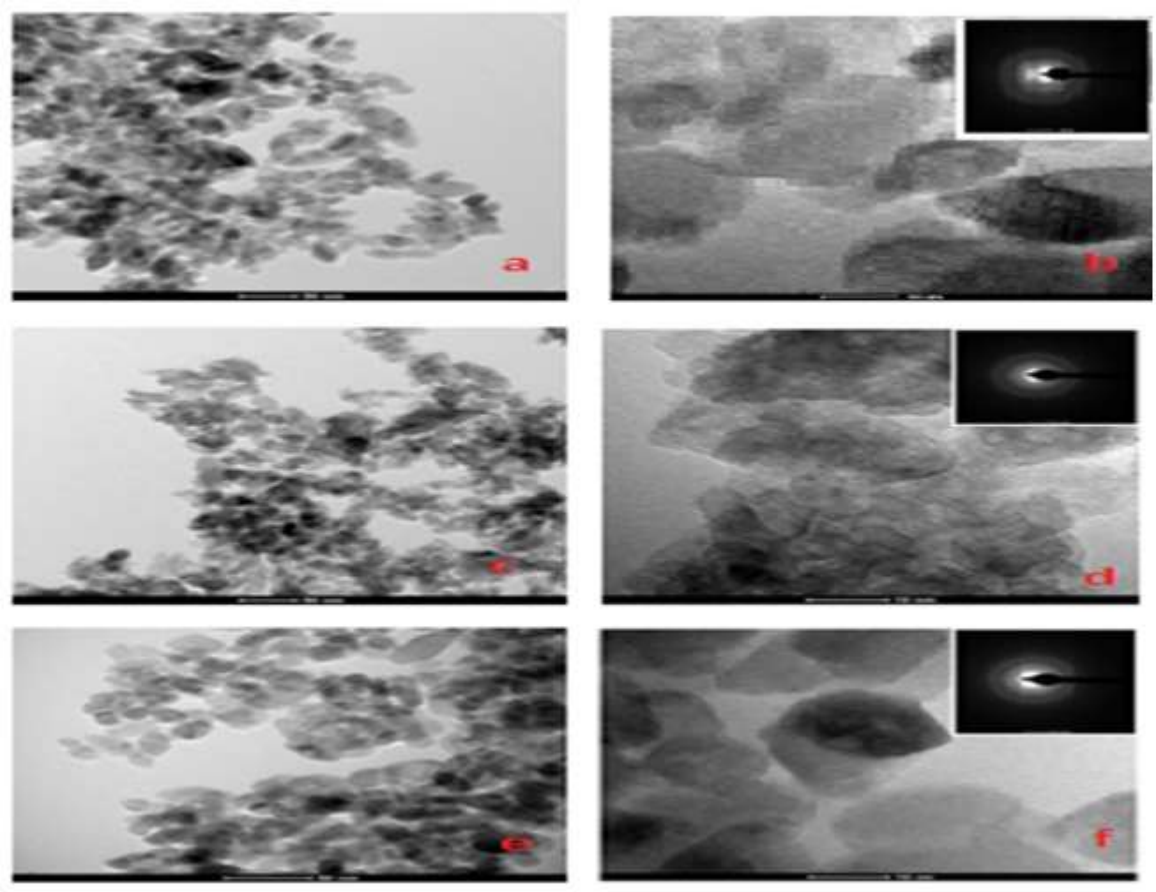

Fig. 5. TEM images of TiO_2powder.

Fig.5 (a, c and e) shows TEM images of hydrothermally synthesized TiO_2 powder (sample-A, B and C) it shows rice grain like structure. Image (b, d and f) shows magnified TEM image and selected area diffraction pattern,it reveals that TiO_2 is predominantly single crystalline anatase with lattice spacing of 0.36nm. The atoms are arranged in definite manner and TiO_2 powder is well crystalline.

F. Sensitivity

Fig. 6 shows that for sample A the sensitivity of thick films was noted20, which is maximum for LPG gas at operating temperature 200^oC against all other tested gases. The thick film of sample-B shows sensitivity 14.11 for H_2 gas at operating temperature 150^oC.The thick film of sample-C shows sensitivity 15 for H_2S gas at operating temperature 350^oC.

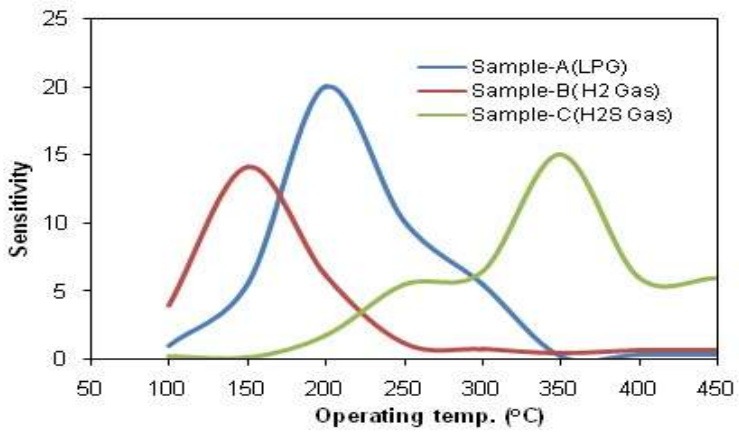

Fig. 6. Sensitivity of TiO_2thick films.

G. Selectivity

Fig.7 shows that the TiO_2 thick film was selective to LPG gas (800 ppm) at 200°C against all other tested gases such as CO, CO_2, H_2, Cl_2, NH_3 and H_2S.

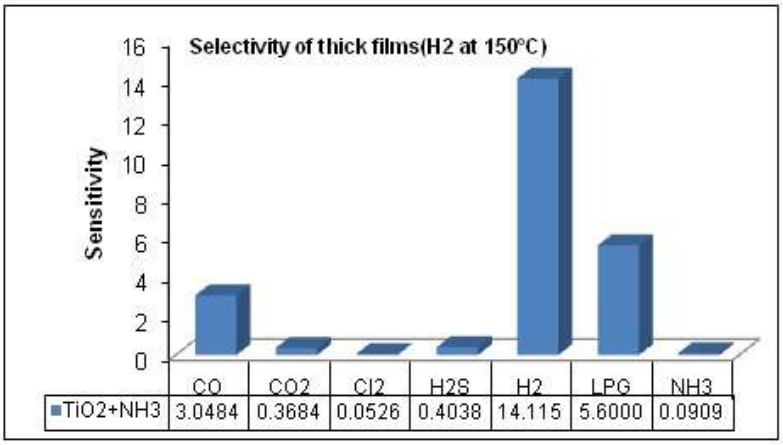

Fig. 7. Selectivity of TiO_2thick film (sample A).

Fig.8 shows that the TiO_2 thick film is selective to H_2 gas (800 ppm) at 150°C against all other tested gases such as CO, CO_2, LPG, Cl_2, NH_3 and H_2S.

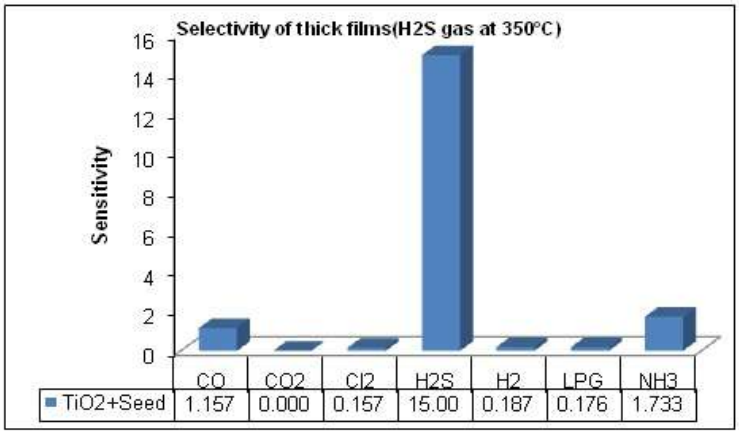

Fig. 8. Selectivity of TiO_2thick film (sample B).

Fig. 9 shows that the TiO_2 thick film was selective to H_2S gas (800 ppm) at 350°C against all other tested gases such as CO, CO_2, LPG, Cl_2, NH_3 and H_2.

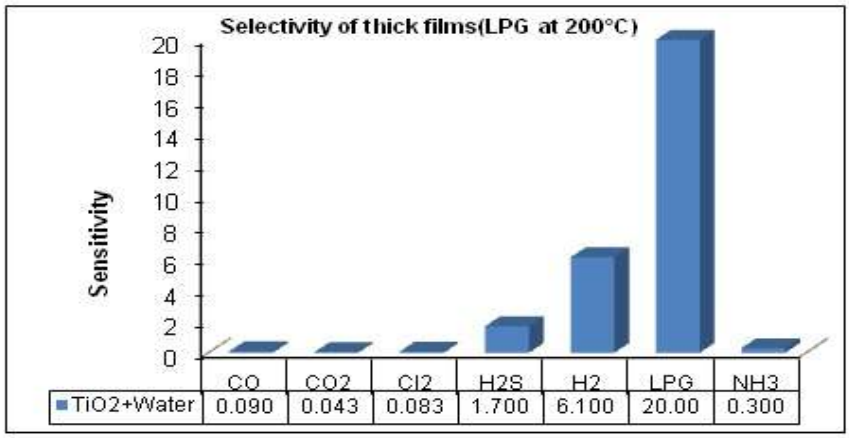

Fig. 9. Selectivity of TiO_2thick film (sample C).

H. Gas sensing mechanism

This is the most commonly accepted model for the operation of a semiconductor gas sensor, which presents a simplified model for a chain of ceramic grains. The physical model shows the grains with adsorbed oxygen on the surface, wherein the adsorbed oxygen has extracted electrons from the subsurface region of the grains leading to an insulating surface layer. In the bulk, however, the electrons are assumed to be plentiful. For conduction to occur, the electrons must pass from one grain to the other through this insulating layer. The Fig. 10 (b) shows the band model depicting this insulating layer in terms of the potential barrier. The extraction of electrons by the adsorbed oxygen from the surface leaves behind positively charged ions and consequently, an electric field develops between the positively charged ions and the negatively charged oxygen ions on the surface. For the conduction, the electrons in the conduction band must overcome the barrier associated with this electric field in order to move to the neighbouring grain. The barrier they must overcome is indicated as qVs, where Vs increases as the concentration of O- increases.

The density of electrons with sufficient energy to cross this barrier is ns, given by the Boltzman equation:
Ns =Ndexp (-qVs/kT)……………………..………… (1)

With Nd the density of donors. The conductance through the film will be proportional to Ns. The more oxygen present on the surface, the higher the barrier and fewer electrons can make the transition and therefore the higher the resistance. The adsorbed oxygen is capable of causing a band bending up to 1eV at high coverages. The theoretically estimated coverage of the negatively charged species on the surface is limited to 1012- 1013 cm^{-2} (Weisz limit). However, the coverage of this species is less than this limit under ambient conditions and hence, the potential barrier is less than 1eV. The overall chemical reactions assumed in this typical model are:

$O_2+2e^-\rightarrow 2O^-$…………………………...………………….(2)
$+ 2O^- \rightarrow RO + H_2O + 2e^-$…………………………...….. (3)

On exposure to a reducing gas (RH_2) the adsorbed oxygen reacts with the gas decreasing the potential barrier. Hence the electrons can overcome the potential barrier and the conductance increases.

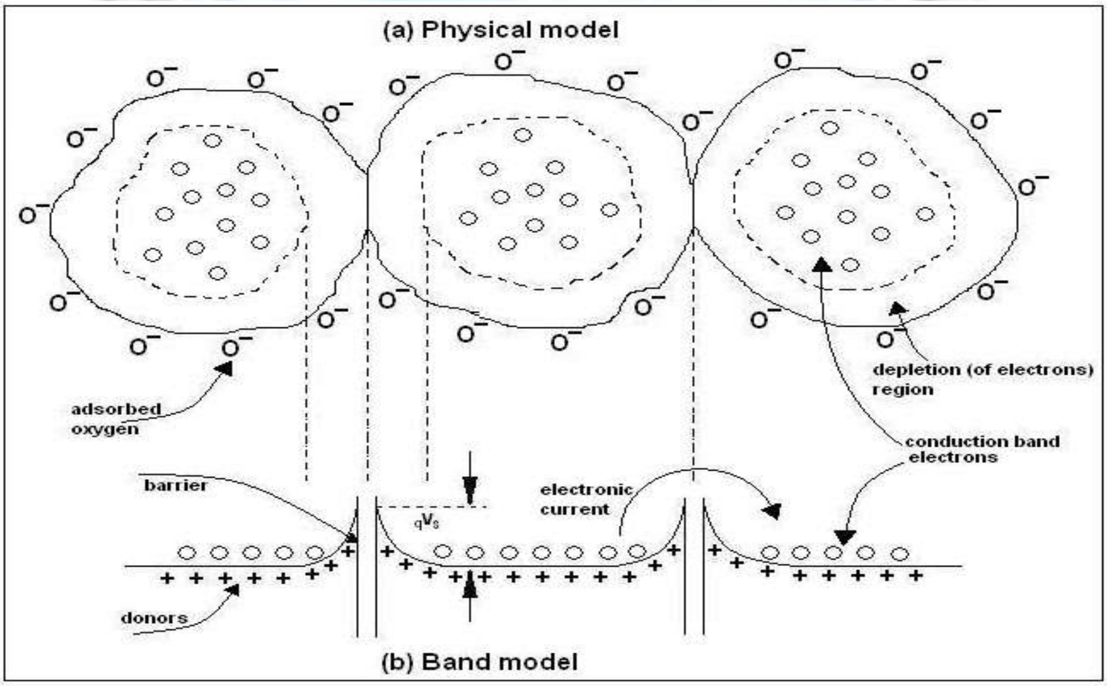

Fig.10. Model indicating the formation of potential barrier on oxygen adsorption.Physical model (a) and band model (b)

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