RECENT TRENDS IN NANOSTRUCTURED MATERIALS FOR GAS SENSING APPLICATIONS

Abstract

For environmental protection and medical applications, there has recently been an increase in interest in the development of quick, sensitive, and focused smart gas sensors. Significant research has been done in the area of sensor technology. However, there are some difficulties. This chapter covers the principles of chemical gas sensors, sensor features, strategies to improve gas sensing performance, factors affecting sensor performance, sensing mechanism, and literature review of gas sensor materials.

Keywords: Gas sensors; Nano materials, sensors, Sensing Mechanism, Surface engineering; Doping; Spillover mechanism.

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I. INTRODUCTION

1. **Background of Nano science and Nanotechnology:** The widely practiced fields of nano-science and technology of today actually arose from the theories of some of the top minds of the previous century. The most well-known of them was Richard P. Feynman. On December 29, 1959 [1] at California Institute of Technology, he gave the renowned speech "there is plenty of room at the bottom" to the American Physical Society's annual general body meeting in which he discussed the notions of manipulating and controlling things at the atomic scale. The great scientist also said in same illustrious lecture that "the principles of Physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom" (among other well-known quotes His plans to create circuits with diameters as small as a few nanometers that could be employed as components in more potent computers were at the time viewed as "too speculative." But almost two decades after Feynman gave this prophetic speech, a number of innovations and discoveries made their debut, supporting his beliefs about the future. The significance of these discoveries was quickly recognized by technological advisers and prognosticators, who predicted that the nanotechnology revolution, like the industrial and information revolutions before it, was about to begin. In his book, "Engines of Creation, the Coming Age of Nanotechnology," Drexler stimulatingly and lateral thinkingly advanced Feymnan's concepts and definition [2]. Drexler's definition of nanotechnology can be summed up as follows: "Nanotechnology is the principle of atom-by-atom manipulation through control of the structure of matter at the molecular level. It requires the capacity to assemble molecular systems with atomic-level accuracy, producing a range of nanomachines.

   In 1998, the National Science and Technology Council (NSTC) of the United States established an integrative working group on nanoscience, engineering, and technology in acknowledgment of this reality. The National Nanotechnology Initiative (NNI) initiative was subsequently announced in 2001 with a sizable amount of funding in the budgetary allocations [3]. The main goal of this programme was to develop a single platform for working on this new technology among academia, industries, and the private sector. Following this lead, the majority of the developed nations as well as several developing nations, such as China and India, made significant investments in research and development in this emerging sector of science and technology [4].

2. **Definition of Nano-science and Nanotechnology:** Neil Armstrong said that the first time he set foot on the moon, it was "a small step for a man and a giant leap for mankind." Nanotechnology might be another huge leap for humanity, but it's a jump so little that compared to it, Neil Armstrong would appear to be the size of a solar system. The word "nano" is derived from the Greek for dwarf, but in scientific parlance, it refers to one billionth. One nanometer, often known as 1 nm, is equal to one billionth of a metre. We frequently use the comparison of a human hair to demonstrate how little a thing is. The typical diameter of a human hair is roughly 50,000 nanometers, so that gives you an idea of the nanoscale. The tiniest features that can now be etched on a commercial microprocessor are less than 100 nm, in contrast. The smallest object that the human eye can resolve without assistance is 10,000 nm in size.

   The study of the fundamental properties of molecules and structures with at least one dimension roughly between 1 and 100 nanometers is the generally accepted definition

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of nano-science. Naturally, these restrictions are not extremely tight. Some could claim that atoms and molecules have been understood by humans for more than a century, and that chemists have been working with them for a very long time. Atoms typically have sizes that are significantly smaller than a nanometer. Therefore, why is nanotechnology currently generating so much buzz? Can we classify all of these atomic or molecular chemistries as nanotechnologies? No, that's not the solution to this query. The most crucial aspect of nano items is whether or not we can detect size dependences in the attributes. The incorporation of these nanostructures into practical nanoscale devices is known as nanotechnology. Nanotechnology is an upcoming industrial technology that enables precise, affordable control of matter structure by interacting with atoms. That definition falls short of what is needed. Understanding that nanoscale is not just about being small but also a particular kind of small will help to explain it. Anything that is smaller than a nanometer, such as a free atom or small molecule floating in outer space as a tiny, diluted speck of vapour, may not be regarded as a nanotechnology object. Nanostructures are therefore not simply smaller than anything we have previously created. Drexler [2] asserts that "nanotechnology is the principle of atom-by-atom manipulation through molecular level control of matter structure. It requires the capacity to assemble molecular systems with atomic-level accuracy, producing a range of nanomachines.

In a useful approach, Binnig and Rohrer developed Drexler's theories. They were the first to observe atoms in 1981, opening the door for nanotechnology. Atoms could soon be picked up and moved by scientists to create structures. The term "nanotechnology" was first only used to refer to these pioneering investigations, which had no immediate use in daily life. However, attention grew once the discovery's importance was understood, and the term has since become more widely used at the nanoscale level [5]. Nanotechnology, which is the science and art of manipulating matter at the atomic or molecular level, has the potential to significantly advance environmental protection technologies.

3. **Application of Nanotechnology:** Nanotechnology descriptions that only highlight the tiny scale of the physical components that it is concerned with It sounds like nanotechnology is just using infinitely smaller parts than normal engineering, assemblies between the size of an atom and around 100 molecule diameters. Working things, on the other hand, are inherently more complicated; rearrangements of the atoms and molecules result in novel features and peculiar behaviors. The behavior of individual atoms and molecules, which is fixed, transitions into the behavior of collectives, which is flexible. In a wide range of academic disciplines, from the fundamental sciences to engineering, many scientists are currently looking into the fundamental nature of nanotechnology. Many areas of established research, such as colloid science, electronics, chemistry, physics, and genetics, will be used, but they will be enhanced by fascinating new discoveries. The possible uses for nanotechnology are extremely diverse. For instance, in medical systems, it would be able to enhance the tissue compatibility of implants to produce artificial organs or scaffolds for tissue regeneration. New genetic therapeutics and anti-aging medications may also be developed in the future. Leading enterprises and industrial research organizations currently utilize nanotechnology for a variety of technical and creative purposes. Examples include [6]:

- Zeolites, minerals with pore smaller than 1 nm, are being used by Exxon Mobil as a more effective catalyst to split or fragment big hydrocarbon molecules into petrol.
- IBM has enhanced disc drives with nanoscale stacking to provide extremely dense data storage by taking advantage of the giant-magneto-resistive effect.
- To treat Kaposi's sarcoma, an AIDS-related malignancy, Gilead Sciences is utilizing nanotechnology in the form of lipid spheres, or liposomes, that are roughly 100 nm in diameter.

Nano phase technologies make use of nano-crystalline particles that are mixed into other materials to create, among other things, strong ceramics, transparent sunblocks, and environmental catalysts. These businesses all use nanotechnology to create more effective, reasonably priced, and most recently, ecologically friendly products, although having quite diverse outputs [7].

II. NANO-MATERIALS

1. **Introduction:** The foundation of nanoscience and nanotechnology is nanomaterials. The study of nanostructures is a large, interdisciplinary field of research and development that has grown rapidly in recent years all around the world. The methods used to create materials and goods, as well as the range and kind of functionalities that can be available, have the potential to be substantially altered. It already has a significant commercial impact, and this influence will likely continue to expand.

   Materials with a minimum dimension of 100 nanometers or less are referred to as nanoscale materials. A nanometer is 100,000 times smaller than the diameter of a human hair, or one millionth of a millimetre. Nanomaterials are fascinating because of the distinct optical, magnetic, electrical, and other properties that exist at this scale. These new qualities have a significant positive impact on the disciplines of electronics, medicine, and other industries.

2. **Source of nanomaterials:** Engineered nanomaterials (EN), which are already employed in many commercial items and processes but certain nanoparticles are manufactured artificially, are of tremendous interest. They are used commercially in items including sunscreen, cosmetics, sporting goods, stain-resistant clothing, tyres, and electronics as well as in medicine for diagnostics, imaging, and medication delivery [8]. Engineered nanomaterials are substances produced at the molecular (nanometer) scale in order to take advantage of their minuscule size and distinctive properties, which are frequently absent from their conventional, bulk counterparts. The two key factors that enable materials to have a variety of properties at the nano scale are an increase in relative surface area and new quantum phenomena. Compared to their traditional forms, nanomaterials have a substantially higher surface area to volume ratio, which can increase their chemical reactivity and weaken them. The properties and features of a material can change significantly at the nanoscale, resulting in unique optical, electrical, and magnetic behaviours. Numerous consumer products, including windows, bicycles, and automobiles, are using nanocoatings and nanocomposites. Longer-lasting tennis balls made of composites of butyl rubber and nano-clay and innovative UV-blocking coatings for glass bottles are also available. Nanoscale silica is used as filler in a variety of items,

including cosmetics and dental fillings [9]. Nanoscale titanium dioxide, on the other hand, is finding applications in cosmetics, sunblock creams, and self-cleaning windows.

3. **Advances in Nanomaterials:** The history of nanomaterials, which extends back to the big bang, begins with the development of nanostructures in the earliest meteorites. Later, many more natural nanostructures, including animal bones and seashells, emerged. The use of fire by early humans led to the creation of smoke particles with a nanoscale. However, it wasn't until much later that the history of nanomaterials in science began. One of the earliest scientific accounts described the production of colloidal gold particles by Michael Faraday in early 1857. Researchers have been researching nanostructured catalysts for more than 70 years. By the early 1940s, precipitated and fumed silica nanoparticles were being created and promoted as an alternative to ultrafine carbon black for rubber reinforcements. Many common consumer goods, including non-dairy coffee creamer, car tyres, optical fibres, and catalytic supports, now use nanosized amorphous silica particles on a wide scale. Metallic nanopowders for magnetic recording tapes were created in the 1960s and 1970s. Granqvist and Buhrman published the first article on nanocrystals made using the now-common inert-gas evaporation method in 1976. Maya blue paint has just been discovered to be a nanostructured hybrid material. The material is formed of needle-shaped palygorskite (clay) crystals that form a super lattice with a period of 1.4 nm, according to studies of real samples from Jaina island. Intercalates of amorphous silicate substrate with metal (Mg) nanoparticle inclusions are also present. The origin of its colour and its resistance to acids and biocorrosion are still unknown. The creation of synthetic samples has demonstrated that the lovely blue hue can only be attained when both these nanoparticles and the superlattice are present. Today, nanophase engineering is used to manipulate the mechanical, catalytic, electric, magnetic, optical, and electronic characteristics of a constantly expanding range of structural and functional materials, both inorganic and organic. The development of distinct tiny clusters that are later fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials is often the basis for the manufacture of nanophase or cluster-assembled materials. The nanophase silicon, which has different physical and electrical characteristics from regular silicon, could be used in macroscopic semiconductor processes to make new devices. For instance, when common glass is doped with quantized semiconductor "colloids," it transforms into a high performance optical medium with potential uses in optical computing [10].

4. **Classification of Nanomaterials:** Nanomaterials are very tiny, with at least one dimension being 100 nanometers or fewer. One-dimensional surface sheets, two-dimensional strands, and three-dimensional particles are examples of nanoscale materials. They come in spherical, tubular, irregular, fused, aggregated, or agglomerated forms. Dendrimers, nanotubes, fullerenes, and quantum dots are typical types of nanomaterials. Nanomaterials with applications in the field of nanotechnology include carbon nanotubes, fullerene, photocatalysts, carbon nano, and silica. These materials are distinct from conventional chemicals in terms of their physical and chemical properties. According to Siegel, there are four different types of nanostructures: zero-, one-, two-, and three-dimensional nanostructures.

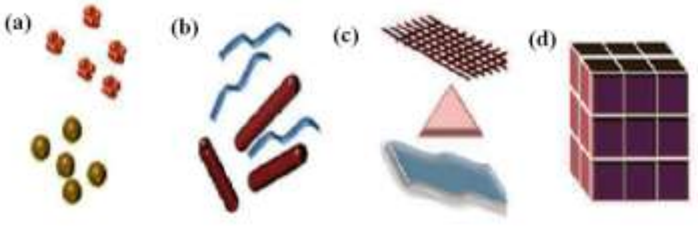

Figure 1: Nanomaterial classification 0D spheres and clusters, 1D nanowire and rods, 2D films, plates, and networks, and 3D nanomaterials are examples of nanostructures.

Nanomaterials are substances with ultra-fine grain sizes (50 nm) or dimensions that are no larger than 50 nm. According to Richard W. Siegel, there are four different modulation dimensionalities that can be used to create nanomaterials: One (multilayers), two (ultrafine-grained over layers or buried layers), and three (nanophase materials made up of equal-sized grains at the nanoscale scale, as seen in Figure 1) are the different types of materials. Zero (atomic clusters, filaments, and cluster assemblies) is the simplest type.

5. **Importance of Nanomaterial:** These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

- Nano-phase ceramics are of particular interest because, in comparison to coarse-grained ceramics, they are more ductile at high temperatures.
- It is well known that nanostructured semiconductors exhibit a variety of non-linear optical characteristics. Quantum confinement phenomena in semiconductor Q-particles can result in unique features, such as luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Solar cells' window layers are made of nanostructured semiconductors.
- Metallic nanopowders have been employed to create porous coatings, dense components, and gas-tight materials. Their ductility and cold welding characteristics make them appropriate for metal-metal bonding, particularly in the electronic industry.
- Individual magnetic nanoparticles are mono-domains, and one would anticipate that the grains in magnetic nanophase materials correspond to domains, whereas the borders are disordered walls. In addition to the superparamagnetism behaviour, very small particles have unique atomic structures with distinct electronic states that give rise to unusual features. Magnetic nanocomposites have been utilised for magnetic refrigeration, high density information storage, and ferrofluids for mechanical force transfer.
- Catalytic applications benefit particularly from nanostructured metal clusters and colloids with mono- or plurimetallic composition. They have been demonstrated to give significant advantages for activity, selectivity, and lifetime in chemical transformations and electro-catalysis (fuel cells), and they may operate as precursors for new types of heterogeneous catalysts (Cortex-catalysts). Using choral modifiers on the surface of nanoscale metal particles, selective catalysis was also accomplished.
- Nanostructured metal-oxide thin films are gaining more attention for the development of gas sensors with improved sensitivity and selectivity for NOx, CO, CO_2, CH_4 and aromatic hydrocarbons. Car or consumer product rechargeable batteries use

nanostructured metal oxide (MnO_2). Nano-structured titanium oxide porous films are employed for their high transmission and large surface area enhancement resulting to strong absorption in dye sensitised solar cells. Nanocrystalline silicon films are used for very transparent connections in thin film solar cells.

- Interesting materials for photonic band gap structuring include polymer-based composites with a high amount of inorganic particles, which results in a high dielectric constant.

III. METAL OXIDE SEMICONDUCTORS

1. **Introduction:** Due to its compatibility, low cost, and small structure, metal oxide semiconductors have drawn interest from the research community [11]. The manufacturing, chemical, and physical properties of metal oxide semiconductors provide excellent results [12–14]. By concentrating on the enhancement of low resistance (resistance in air), high sensitivity and selectivity, with quick response and recovery, the examination of a good metal oxide gas sensor is done [15]. These variables are greatly influenced by the surface's morphology, including the grain size, surface area, shape, dimension, and grain network or porosity [16]. Therefore, cutting-edge research is done to enhance the active layer's ability to sense by adding catalyst, doping metals and metal oxides, reducing grain size, and managing pore and surface imperfections. Due to its outstanding sensing capabilities when exposed to both reducing and oxidizing gases, tin oxide is used in many research projects [17, 18].

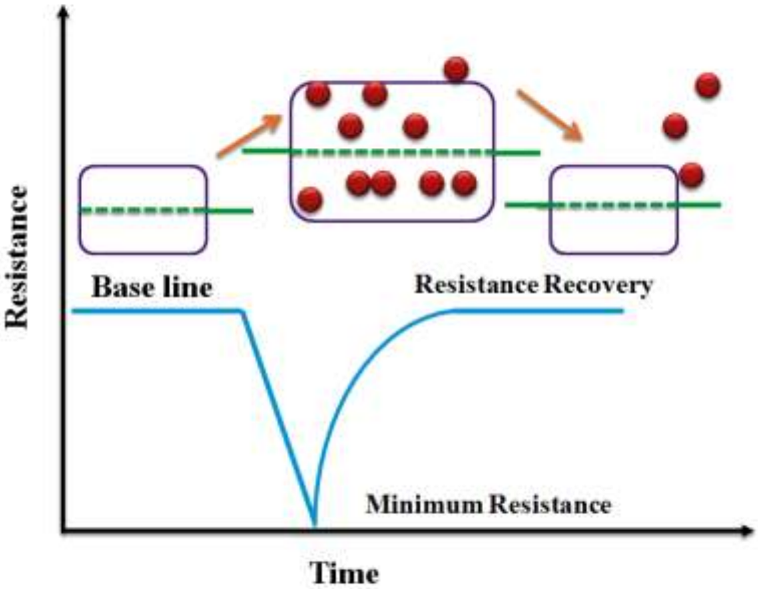

Figure 2: Gas sensing mechanism in metal oxide semiconductors

The semiconductor gas sensors are ideal for many developing applications because of their great sensitivity, selectivity, and functional simplicity. At the semiconductor's surface, chemical reactions and charge transfer from or to gas molecules can happen quickly, changing the charge carriers' density [19]. Based on the interaction of the gas with the semiconductor surface, the gas sensors' detecting mechanism functions at the metal oxide film's grain boundary, as shown in Figure 2 Catalytic effects, surface chemical reactions between various adsorbed chemical species, semiconductor reduction or oxidation, gas molecule adsorption on the semiconductor surface, and adsorption by chemical reaction with the surface layer that is related to the pre-adsorbed oxygen are all components of the sensing mechanism. Figure 3 displays the processes that take place in the metal oxide during gas detection, along with their results.

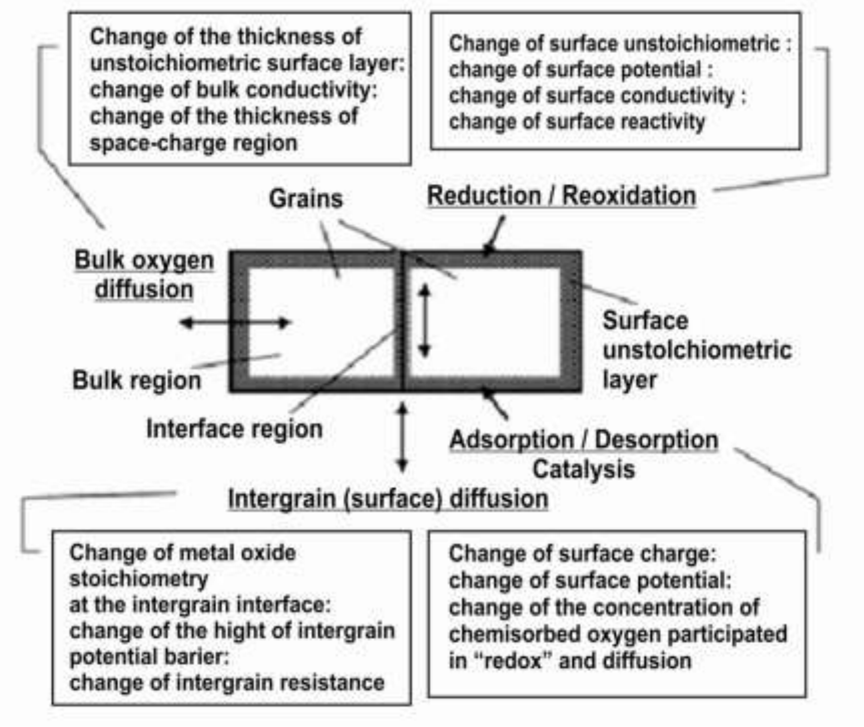

Figure 3: The processes that occur in metal oxide during gas detection and how they affect the characteristics of polycrystalline metal oxide

When exposed to oxidizing or reducing gases, the surface processes, which are reversible, drastically change the electrical conductivity. Chemical species in the environment can be found using a change in electrical conductivity. Several models that have been previously described [26–28] are the foundation for how surface-based reactions affect the sensor's response. Metal oxide semiconductors like tin oxide and indium oxide are used as gas sensors based on the sensing mechanism that a change in electrical resistance occurs as shown in Figure 4 due to the interaction between reducing or oxidizing gas and the chemisorbed oxygen species such as O and O_2 [29, 30]. Charge is electrically transferred from the conduction band to the oxygen species on the surface when O_2 is adsorbed onto the surface of a semiconducting metal oxide. The surface area acts as a depletion region by losing electron density. When exposed to a reducing environment, such as carbon dioxide, a chemical reaction between the exposed gas molecules and the negatively charged adsorbed oxygen species occurs on the surface. This chemical reaction then results in the return of electrons to the surface, increasing conductivity. The gas sensing method heavily depends on the chemical interaction between the surface-chemisorbed species and the exposed gas [31].

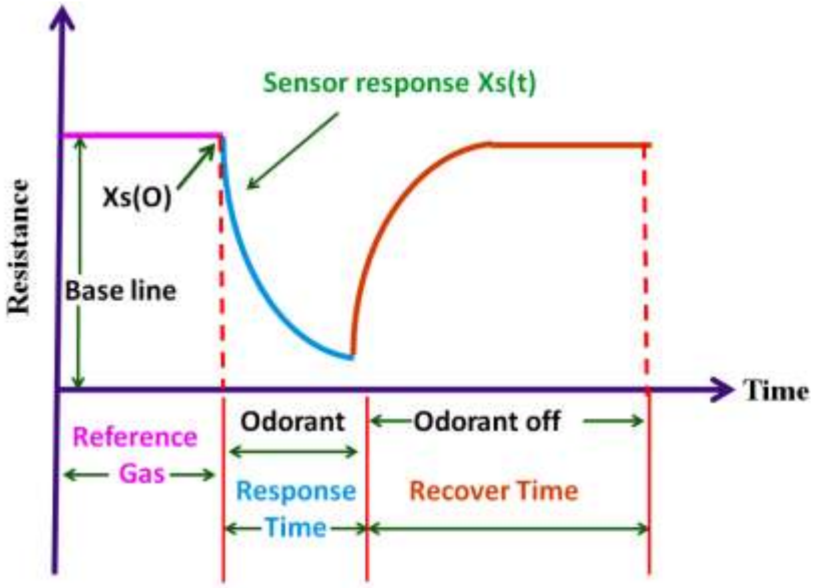

Figure 4: Gas sensing mechanism in metal oxides

Nano-scale catalysts are put on the surface of the sensing element to boost its response to the detection of reducing gases. The active oxide is well supported in catalysis by the catalyst placed on it. The area of the interfacial connection is significantly increased by the presence of nanoparticles. Additionally, increasing catalyst dispersion, the mean surface diffusion distance between nanoparticles and chemisorbed oxygen species reduces [32]. Tin oxide is the metal oxide semiconductor that was used in this experiment.

2. **Working Principle:** Thick films of metal oxides like ZnO, SnO_2, WO_3 etc. when heated in the range 2000C to 4000C in air sensitively respond to a wide range of oxidizing and reducing analyte gases via conductivity changes. The steps involved in the sensing process are detailed below;

- Diffusion of reactants to the active region
- Adsorption of reactants on to active region
- Surface reaction
- Desorption of products from active region
- Diffusion of products away from active region.

The ambient temperature of the measure and atmosphere, which is typically considered to be room temperature, determines how quickly reactants diffuse in the active zone. Gas molecules have a tendency to stick to the detecting surface once they have diffused into the active layer. Adsorption is the name of this process. There are two different types of adsorption: physisorption and chemisorption. In the case of physisorption, only weak physical forces (Van der Waals-type forces) are used to bind the species to the surface. The electron density between the surface and the adsorbed gas is rearranged via chemisorption bonds. The atoms on the surface are not perfectly coordinated when a solid is terminated by a surface. There are "dangling bonds" that are unfulfilled, that are not shared with neighbors, and one or two of the closest neighbors are missing [33]. Particularly, both cations and anions exhibit weak coordination in an ionic crystal like SnO_2. A thin layer of negatively charged oxide ions surrounds the positively charged Sn ions on the surface. The following describes a model initially proposed by H. Windischmann et al [34] for rationalizing the behavior of the sensor in the measure and environment.

$\frac{1}{2} O_2 + e^{-} \Leftrightarrow O_{ads}$ ..... (1.1)
$R(g) + O_{ads} \rightarrow RO(g) + e^{-}$ .... (1.2)

On the surface, oxygen adsorbs and then dissociates to create O. This O pulls an electron out of the semiconductor. This electron extraction causes a depletion area to form close to the surface, which raises the gas sensor's resistance (for n-type semiconductors). Figure 5 depicts a three-dimensional image of an oxygen-adsorption-induced crystallite of gas-sensitive material. Additionally, the charged double layer development near the surface is blamed for the band bending near the surface [35]. Figure 6 provides greater clarification on the band bending.

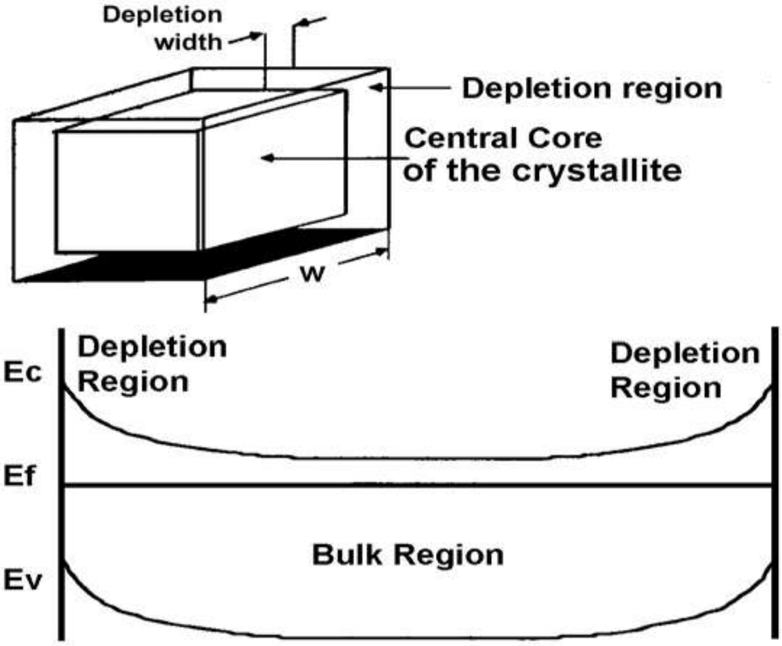

Figure 5: 3-D rendering of crystallite depletion at a certain temperature and in the presence of ambient oxygen. Also included is a corresponding energy band diagram.

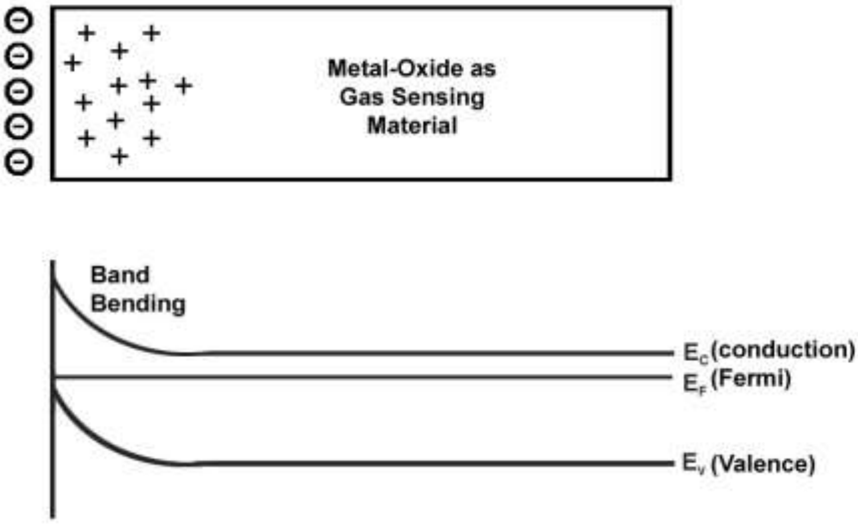

Figure 6: Charge distribution and energy band diagram for an oxygen chemisorption surface using an n-type metal-oxide gas sensing material

The resistance tends to decrease when a flammable gas, such as hydrogen, is present because the gas combines with the adsorbed O to generate water, and the electron is then injected back into the semiconductor. The removal of electrons by oxygen and their restoration by combustible gases compete for dominance [36]. The steady state value of the resistance is dependent on the concentration of the combustible gas since the oxygen content in the atmosphere is constant. The contrasting responses are shown below [37].

$$O_2 + 2e^{-} \rightarrow 2O^{-}_{ads} \qquad \text{..... (1.3)}$$

$$H_2 + O^{-}_{ads} \rightarrow H_2O + e^{-} \qquad \text{..... (1.4)}$$

The combustible gas, if chemically active, removes lattice oxygen from the metal oxide is another scenario that might exist or coexist. As a result, vacancies are created that serve as donors. Reoxidizing oxygen with air has the tendency to eliminate donor vacancies. As a result, the donor vacancies that remove oxygen and those that produce combustible gas are in competition with one another. Since oxygen pressure is constant, the density of donor vacancies (and hence the resistance) depends only on the concentration of combustible gas. Below [38] is an illustration of this.

$$CO + M^{2+} + O_L^{2-} \rightarrow CO_2 + M^{2+} + 2e^{-} \qquad \text{.... (1.5)}$$

Where M is the metal cation and OL is the lattice oxygen. Thus, for reducing and oxidising analyte gases, two distinct kinds of semiconductor gas sensor operating processes may be identified. The surface reaction of a reducing gas with adsorbed oxygen causes changes in conductance due to the extraction and re-injection of electrons from the film in the first class. The second involves the combustion of combustible gas, which removes oxygen from the lattice and creates donor vacancies. The semi-conducting film's conductance changes as a result of the donor vacancies, which in turn inject carriers into its conduction band. Adsorbed gas has three possible outcomes after being detected by a

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gas sensor: it can either stay there eternally (at low temperatures), interact with the material used to detect the gas (sensor poisoning), or desorb and re-diffuse into the atmosphere. Desorption is the separation of an atom or molecule from a surface. Desorption is a thermally stimulated process, just like adsorption. The sensor is prepared for the following measurement when the gas desorbs and diffuses away from the sensor surface. Dead time refers to the time that the sensor is not operational.

IV. CRYSTAL STRUCTURE OF SnO_2

Due to its great optical transparency, relative electrical conductivity compared to other oxide ceramics, excellent chemical and mechanical stability, and high optical conductivity compared to other oxide ceramics, tin oxide (SnO_2) in both its pure and doped forms is well-known as a transparent conductor [39]. The so-called cassiterite (mineral form) or rutile (material structure) phase of SnO_2 is the only stable phase. It forms a tetragonal rutile structure with space group (P42/mnm), which is listed as number 136 in the rutile structure standard listing.

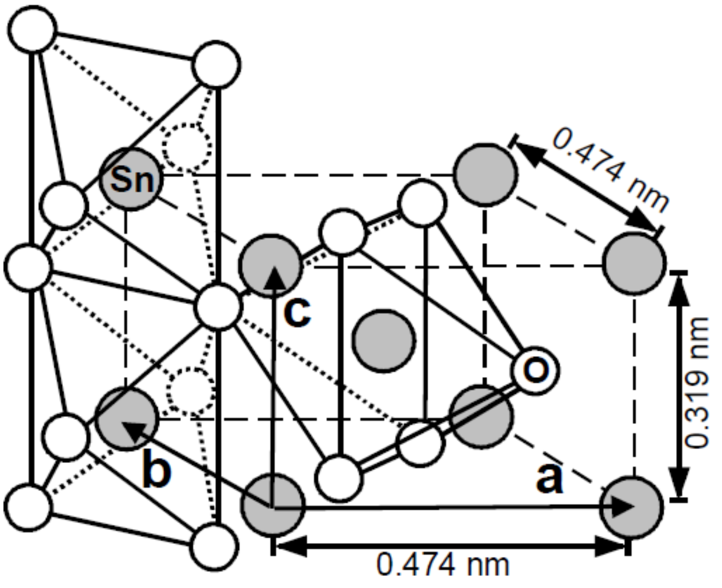

Figure 6: Unit cell of SnO_2 with four O^{2-} anions and two Sn^{4+}cations.

Six atoms make up its unit cell: two tin atoms and four oxygen atoms. Six oxygen atoms put roughly at the corners of a normal, slightly distorted octahedron surround each tin atom, creating a 6:3 coordination [40] (Figure 6). Three tin atoms placed roughly at the corners of an equilateral triangle surround each oxygen atom. As a result, it is the 6:3 co-ordinations structure. A=b=4.737 and C=3.185 are the lattice parameters. 0.673 is the c/a ratio [41, 42]. O^2 and Sn^{4+} have ionic radii of 1.40 and 0.71 respectively. The oxygen atoms (anions) are situated at positions (u, u, 0) and (1/2+u, 1/2u,1/2), where the internal parameter, u, has the value 0.307, while the metal atoms (cations) are situated at positions (0, 0, 0) and (1/2, 1/2, 1/2) in the unit cell. Each cation has four anions at a distance of $[2(1/2u)^2+(c/2a)^2]1/2a$(2.597) and two anions at a distance of 2ua (2.053). The substance has a heat capacity of 52.59 J mol^{-1} K^{-1}, a density of 6.95 g cm^{-3} at 300 K, and a melting point of

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1630^{o}C. The associated heat of production is H = 1.9 103 J mol^{-1} [43].Some of the chemical and physical characteristics of SnO_2 are listed in Table 1.

Table 1: Physical and Chemical parameters of Tin Oxide

Molecular formula	SnO_2
Molecular mass	150.71 g/mol
Density	6.95 g/cm^3
Melting point	1630 °C
Solubility in water	Insoluble
Appearance	White powder
Crystal structure	Rutile (Tetragonal)
Semiconductor type	n-type

V. GAS SENSING PARAMETERS

1. **Response:** Response is a feature of a device that detects changes in the sensing material's physical and/or chemical properties as a result of gas exposure. The relative change in the thick film's resistance is referred to as the response in the context of resistive gas sensors. It is the ratio of the thick film's resistance to that of a specific gas environment [44, 45].

2. **Operating temperature:** All measurements should be made at various temperatures because semiconductor sensor properties are likely to be extremely temperature sensitive. The target temperature range is selected during the preliminary work and varies for various oxides and analyte gases. Conductance takes a while to achieve steady state for some electronics, especially at lower temperatures. Therefore, it is necessary to wait until the conductance has reached a constant value for a sufficient period of time at a certain temperature before taking measurements. Additionally, it has been proposed that the sensor's behavior may be slightly influenced by its recent past. Therefore, it is advised to collect data when the temperature is both rising and falling over the relevant range, at least in the beginning. In order to characterize a sensor and determine the ideal operating temperature where response is greatest, the fluctuation of response with operating temperature is typically used.

3. **Selectivity:** Selectivity has to do with how well a gas-sensing gadget can distinguish between different types of gases. In other words, selectivity is the ratio of a sensor's ability to detect something of interest compared to an uninteresting object. Unfortunately, the metal oxide gas sensor's selectivity is wide, reacting to all reducing gases that react with oxygen on the sensor's surface. According to this architecture, catalytic additives can increase the sensor activity by selectively encouraging a desired chemical reaction in a predetermined region. Additionally, the right catalytic component alters the temperature at which the sensing material responds to the intended target gas. By adjusting a variety of parameters, including as dopants, grain size, catalysts, external filters, operating temperature, and many others, selectivity is frequently tuned and modified to the analyte(s) of interest [46].

4. **Stability:** It is a property that considers the repeatability of the device measurements across time. Many producers subject these materials to a thermal pre-treatment, which

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would lessen subsequent material instabilities, in order to prevent the impacts of non-repeatability after repeated use. In order to prevent instability during their working life, samples are continually heated at 200°C to 400°C during these treatments. Samples are then subjected to high calcination temperatures (400°C to 1000°C for 1 to 8 hrs).

5. **Robustness:** The term "robustness of the sensor" refers to the sensor's capacity to carry out its intended function in a variety of environmental conditions, such as humidity, temperature, etc., over a period of time, and even in the face of drift and stability fluctuations. Unfortunately, the chemical sensor technology settings that can be changed to increase robustness are frequently the same factors that lead to a reduction in responsiveness and selectivity [47]. For instance, a chemical sensor whose reactions are completely irreversible is frequently the most sensitive. Both engineering and science can be used to fine-tune the robustness and sensitivity.

6. **Response and recovery time of the sensor:** When a sensor is exposed to a reducing or oxidizing gas, the response time is the amount of time needed for the sensor's resistance to completely change (typically 90% of its final value). A low response time value indicates a good sensor. When a sensor is exposed to air, the recovery time (typically 90% of final value) is the amount of time needed for the sensor resistance to return to its initial resistance. A low recovery time value is a sign of a good sensor.

7. **Sensor range:** Response or calibration curve is produced when response is plotted versus gas concentration. It is employed to determine the sensor's linearity and saturation level (sensor range). The smallest concentration increase or lowest levels of chemical concentration that can be detected in the sensing environment are both referred to by this phrase.

VI. METHODS TO IMPROVE THE SENSOR CHARACTERISTICS

1. **Use of Catalyst:** To speed up the reaction and boost response, a catalyst must be put on the surface of the film in metal oxide gas sensors. A catalyst is a substance that speeds up chemical reactions without altering itself. Although the reaction's free energy is unaffected, the activation energy is reduced. Gas sensors are meant to benefit from catalysts' quick response time and selectivity, which they do [48]. With the exception of the fact that in gas sensing one is more interested in the reactants than in catalysis, as shown in Figure 7, the catalytic surface reaction used for gas sensing brings this field close to that of heterogeneous catalysis. This method is thought to be very common in disciplines like heterogeneous catalysis, although it has only recently been used sparingly in relation to solid-state gas sensors.

   The sensor's selectivity is influenced by the catalyst that is used. In a perfect world, a catalyst combination that only catalyzes the oxidation of the gas of interest and not any other gas would be used to detect a specific gas in a mixture of gases [49].

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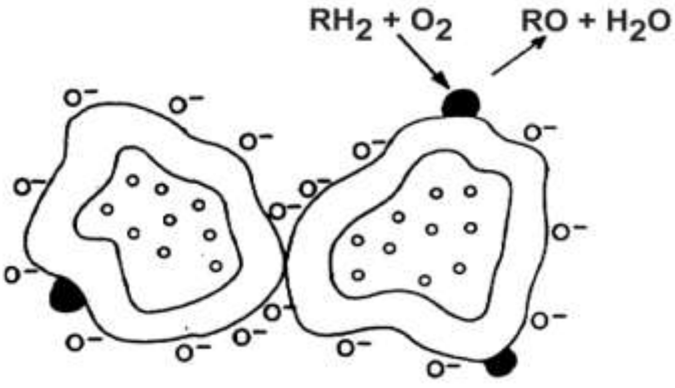

Figure 7: An example of the catalyst effect. Higher surface area nanoparticles function as catalysts. R stands for reducing gas in this context.

Unfortunately, it is difficult to find such perfect mixtures [50]. Semiconducting oxides, like SnO_2 or ZnO are often used as gas sensors because of their wide range of conductance variability and ability to detect both oxidizing and reducing gases. The semiconducting metal oxide is frequently mixed with trace amounts of noble metal additions, such as Pd or Pt, which operate as activators or sensitizers to increase gas selectivity, sensitivity, and reduce working temperature [51, 52]. Catalysts can influence the inter-granular contact region and subsequently the film resistance in one of two ways.

The spillover mechanism and Fermi energy control are the two. A catalyst mechanism that predicts or explains sensor behavior in many contexts has not been developed using catalytic theory, such as spillover and Fermi energy control [53]. Despite all the work that has been done, a thorough investigation of the material-gas interaction and how it affects the electrical response of the sensor is still needed to fully comprehend the impact that additives have on the gas sensing mechanism. The production of activated charge carriers and their tunneling through potential barriers have been used to explain a concept for an enhancement in sensitivity utilizing nanoparticles [54].

2. **Controlling the Grain Size:** The microstructure of polycrystalline elements is one of the key elements that influence how semiconducting gas sensors sense their environment. Each semiconductor oxide crystallite in the element has an electron-depleted surface that extends into the air L times deeper than its surface, where L is a function of the Debye length and the strength of chemisorption. The element's gas sensitivity to the reducing gas will alter with D if the crystallite's diameter D is comparable to 2L since the entire crystallite is electron-depleted. The grain boundary contact or neck that binds the crystallites in the gas sensing elements to their neighboring crystallites. The electrons should pass a potential barrier in the case of grain boundary contacts, the height of which varies with the surrounding atmosphere. In this instance, grain size has no bearing on the gas sensitivity. Electrons travel through the channel that pierces each neck in the case of conduction through necks. The surface space charge layer attenuates the channel's aperture. The neck size of this model relates to the grain size. Yamazoe et al [55] conducted experiments to discover that the neck size has a proportionality constant of 0.8 0.1 to D. The grain boundary control (grain boundary conduction) dominates the conduction of electrons in the sensing element for D>>2L. Neck control serves as the main method for conductivity modulation in D2L. As a result, sensitivity for D2L is

controlled by the grains themselves (grain control) because the electrical resistance of the grains dominates the sensor's overall resistance [56]. The effects of grain size are illustrated in Figure 8 and 9.

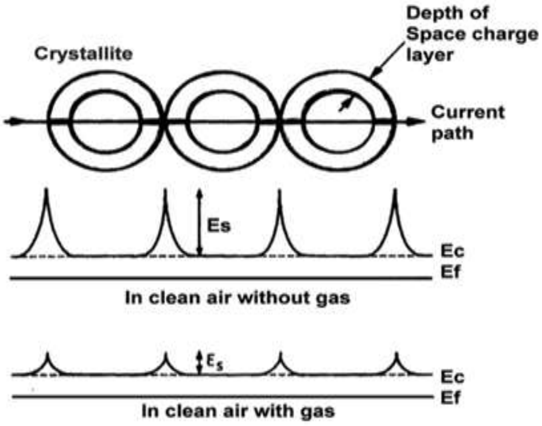

Figure 8: The sensing film's crystallite size is larger than the depletion width, which leads to incomplete grain depletion. The energy barrier for electrons is also depicted in the figure, in both the presence and absence of gas.

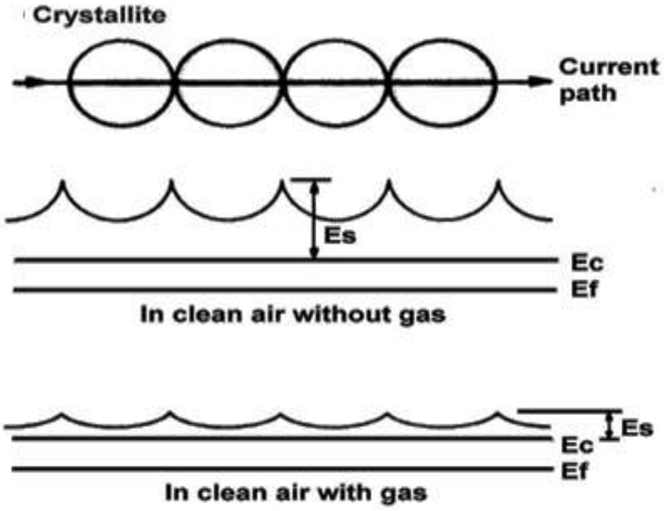

Figure 9: The sensing film's crystallite size matches the depletion width, completely depleting the grain. The energy barrier for electrons is also depicted in the figure, in both the presence and absence of gas.

3. **Temperature Modulation:**The temperature affects the sensors' response and recovery times. Different static properties at various temperatures are caused by temperature-dependent surface covering, co-adsorption, chemical breakdown, or other interactions. On the other hand, the physical characteristics of the semiconductor sensor material, such as the charge carrier concentration, Debye length, work function, etc., are influenced by temperature. The temperature range where, the material is able to catalytically decrease or oxidize the target gas while also modifying the electrical characteristics of the sensor material is the ideal range for a successful sensor response. The precise reducing agent

under investigation affects the rate of response. It is discovered that the sensitivity peaks with a specific lowering agent. If the temperature is too high, the overall oxidation reaction proceeds so quickly that the concentration of reducing agent I at the surface becomes diffusion limited and the concentration seen by sensor approaches zero [57–59]. If the temperature is too low, the reaction rate is too slow to give a high sensitivity. At these temperatures, it is possible to decrease or oxidize the entire target gas concentration that reaches the material surface without observable electrical changes to the metal-oxide material. Once more, the sensitivity is low. On the other hand, temperature needs to be high enough to support gas reaction on the surface of the material. Empirically, the operating temperature is selected to offer the highest sensitivity to the specific gases. Therefore, a thorough understanding of the interaction between the sensing material, catalytic properties, and the sensor electrical response is crucial to comprehending the overall gas sensing mechanism [60]. For each sensor-gas combination, an optimal temperature must be selected from among these ranges. When additional degrees of selectivity are needed, sensor arrays (sometimes referred to as "electronic noses") are utilized, where the multiple sensor's responses are compared for patterns to determine the species of gas. The lack of selectivity of the single metal-oxide gas sensor can also be resolved with such a sensor array by processing the signals of the same type of sensor devices at different operating temperatures or of the device employing different materials at the same temperature [61–62].

VII. LITERATURE REVIEW OF GAS SENSOR MATERIALS

1. **LPG gas sensors:** Liquefied petroleum gas (LPG), a widely utilized but potentially dangerous gas, must be found since it may mistakenly or unintentionally leak and create an explosion. According to various factors, such as operating temperature, greatest gas response, and varied concentrations, different gas sensor materials that have been employed for LPG detection are listed in Table 2.

Table 2: LPG gas sensors materials

Material	$T_{op.}$ (°C)	Sensitivity	Concentration (ppm)	Reference
ZnO	400	43	0.4 Vol. %	[59]
$NiFe_2O_4$-CO-Mn	180	100 %	1000	[46]
TiO_2-Pd	240	35	1000	[48]
ZnO-Cr_2O_3	350	46	100	[53-54]
$BiFeO_3$-Mn	250	7.2	1000	[56]
Pd-SnO_2	325	98%	1.6 Vol.%	[62]
SnO_2	190	340	400	[63]
SnO_2	350	25	600	[64]
ZnO	250	88.2	1.6 Vol. %	[65]
SnO_2	325	14.4	1000	[66]
ZnO-Al	325	89	1 Vol. %	[67]
SnO_2-Cu	264	0.79	500	[68]
SnO_2	274	0.511	500	[69]

2. **NH_3 Gas Sensors:** Ammonia is widely used in a variety of chemical industries, fertilizer plants, cooling systems, etc. Health risks can be caused by a system leak. Ammonia is toxic and damaging in nature. Ammonia exposure damages the respiratory system by irritating and even burning it, among other things. As a result, ammonia gas detection is essential. The different gas sensing components utilised for NH_3 gas sensing are shown in Table 3.

Table 3: NH_3 gas sensors materials

Material	**T_{op}(°C)**	**Sensitivity**	**Concentration (ppm)**	**Reference**
ZnO-RuO_2	250	386	1000	[70]
ZnO-CuO	400	35	1000	[71]
Au-MoO_3-WO_3	400-500	11	1-50	[72]
ZnO-Fe_2O_3	350	573	300	[73]

3. **Ethanol gas sensors:** Most of the use of ethanol is made in the beverage, industrial, and scientific fields. Ethanol is a poisonous gas that induces hypnosis (sleep). Alcohol intake and heavy exposure, especially by smokers, raise the risk of upper respiratory and gastrointestinal cancer. Liver cancer results from alcohol-related cirrhosis. Alcohol exposure or use increases the risk of breast cancer in women. Those who work on the production of ethanol have a high risk of developing cancers of the digestive and respiratory tract. As a result, there is a high demand for ethanol gas monitoring and new issues that are emerging. The several reported materials for ethanol vapour sensors are displayed in Table 4.

Table 4: Ethanol vapour sensors materials

Material	**T_{op}(°C)**	**Sensitivity**	**Concentration (ppm)**	**Reference**
TiO_2	400	36	2000	[74]
Al_2O_3doped ZnO	300	73	1000	[75]
WO_3	400	1424.6 %	50	[76]
SnO_2-pd/pt	450	560	1000	[77]
ZnO	275	12.5	100	[78]
ZnO	400	801	250	[79]
Ga-doped NiO nanoparticles	250	120	10	[80]
SnO/rGO	170	4.76	5	[81]
WO3 nanoflake	250	20.5	50	[82]

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