Review

Metal Oxide Semi-Conductor Gas Sensors in Environmental Monitoring

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Abstract: Metal oxide semiconductor gas sensors are utilised in a variety of different roles and industries. They are relatively inexpensive compared to other sensing technologies, robust, lightweight, long lasting and benefit from high material sensitivity and quick response times. They have been used extensively to measure and monitor trace amounts of environmentally important gases such as carbon monoxide and nitrogen dioxide. In this review the nature of the gas response and how it is fundamentally linked to surface structure is explored. Synthetic routes to metal oxide semiconductor gas sensors are also discussed and related to their affect on surface structure. An overview of important contributions and recent advances are discussed for the use of metal oxide semiconductor sensors for the detection of a variety of gases—CO, NO_x, NH_3 and the particularly challenging case of CO_2. Finally a description of recent advances in work completed at University College London is presented including the use of selective zeolites layers, new perovskite type materials and an innovative chemical vapour deposition approach to film deposition.
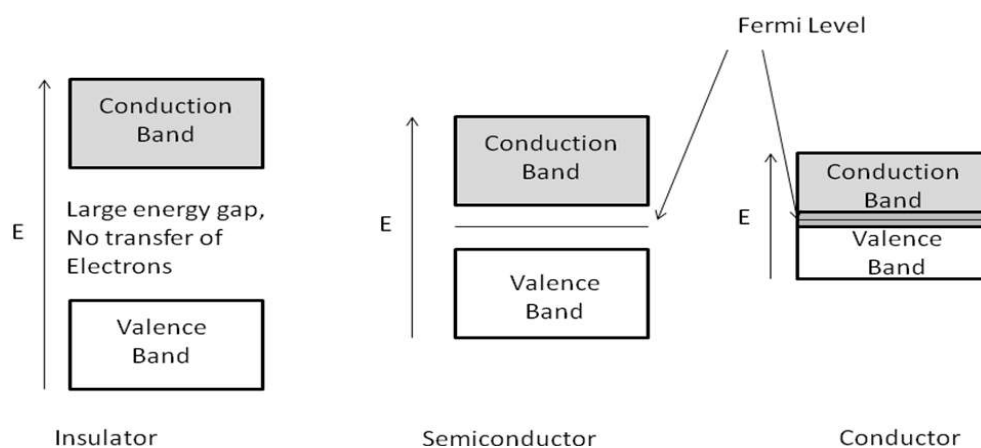
1. Introduction

Since 1962 it has been known that absorption or desorption of a gas on the surface of a metal oxide changes the conductivity of the material, this phenomenon being first demonstrated using zinc oxide thin film layers [1]. The sensitivity of a surface to a gas can be as low as parts per billion (ppb) [2-5]. It is highly desirable that metal oxide semiconductor sensors have a large surface area, so as to adsorb as much of the target analyte as possible on the surface, giving a stronger and more measurable response (especially at low concentrations). Advances in fabrication methods have enabled the production of low-cost sensors with improved sensitivity and reliability compared to those formed using previous methods [6]. Production costs are kept low due to the simplicity of metal oxide semiconductor sensor devices. Their ability to be produced quickly and on a large scale with easily controllable processes makes them a desirable technology to exploit. This paper aims to: (i) introduce the fundamental reasons for sensing gases, (ii) discuss sensor response mechanisms in metal oxide semiconductor sensors, and (iii) show how non-target gases can interfere with the response of such a sensor. The review will then present a summary of recent advances on sensors that have been developed for specific gases such as carbon dioxide and carbon monoxide, and in the final section discuss new approaches developed in our labs at University College London such as the ways in which zeolites can be used to increase specifity, selectivity and efficiency of sensors.

1.1. Basic Theory

1.1.1. Band Theory

Band theory states that within a lattice there exists a valence band and a conduction band. The separation between these two bands is a function of energy, particularly the Fermi level, defined as the highest available electron energy levels at a temperature [7]. There are three main classes of material in band theory (see Figure 1).

Figure 1. Schematic band diagrams of an insulator, semi-conductor and conductor—Note the small gap in the semiconductor, where electrons with sufficient energy can cross and the overlapping of the bands in the conductor.

Insulators have a large gap between the valence and conduction band (typically taken to be 10 eV or more), as such a lot of energy is required to promote the electron in to the conduction band and so electronic conduction does not occur. The Fermi level is the highest occupied state at T = 0 [8]. Semiconductors have a sufficiently large energy gap (in the region of 0.5–5.0 eV) so that at energies below the Fermi level, conduction is not observed. Above the Fermi level, electrons can begin to occupy the conduction band, resulting in an increase in conductivity. Conductors have the Fermi level lying within the conduction band.

1.1.2. Band Theory Applied to Sensors

Band theory as applied to gas sensors has been the subject of intense study for a number of years [9-11]. The target gas interacts with the surface of the metal oxide film (generally through surface adsorbed oxygen ions), which results in a change in charge carrier concentration of the material. This change in charge carrier concentration serves to alter the conductivity (or resistivity,) of the material. An n-type semiconductor is one where the majority charge carriers are electrons, and upon interaction with a reducing gas an increase in conductivity occurs. Conversely, an oxidising gas serves to deplete the sensing layer of charge carrying electrons, resulting in a decrease in conductivity. A p-type semiconductor is a material that conducts with positive holes being the majority charge carriers; hence, the opposite effects are observed with the material and showing an increase in conductivity in the presence of an oxidising gas (where the gas has increased the number of positive holes). A resistance increase with a reducing gas is observed, where the negative charge introduced in to the material reduces the positive (hole) charge carrier concentration. A summary of the response is provided in Table 1.

Table 1. Sign of resistance change (increase or decrease) to change in gas atmosphere [6].

Classification	Oxidising Gases	Reducing Gases
n-type	Resistance increase	Resistance decrease
p-type	Resistance decrease	Resistance increase

1.2. A Model for Gas Interaction
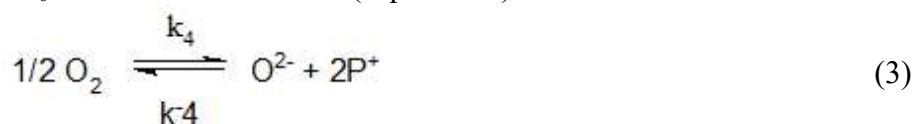
1.2.1. A p-Type Sensor Response

A simple model for the response of a p-type sensor is demonstrated by Equations 1 and 2; showing the adsorption of an oxygen atom to the surface of the material, causing ionisation of the atom and yielding a positive hole (p^+), demonstrated by (1). The positive hole and the ion can then react with a reducing gas such as carbon monoxide, forming carbon dioxide (k_2) or be removed through interaction with each other (k_{-1}) [12] (2) The difference in charge carrier concentration (in this case the positive hole) is manifest in a resistance change between the sensor's electrodes and read by the measurement circuitry:

$$\frac{1}{2}O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O^- + p^+ \tag{1}$$

$$p^+ + O^- + CO \xrightarrow{k_2} CO_2 \tag{2}$$
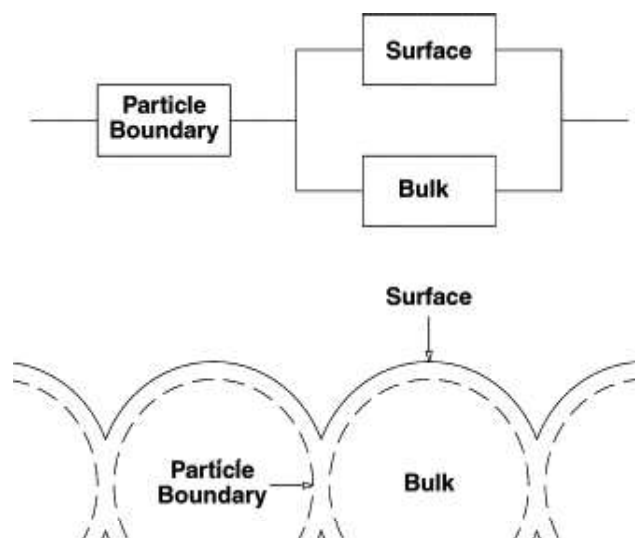
1.2.2. The Equivalent Circuit Model

The response model, as described by Naisbitt [13] *et al.*, which includes the influence of sensor microstructure is a refinement of the conventional response model that is found to apply of over a limited range of examples only, and assumes that the absorbed species on the surface of the metal oxide is the O^{2-} species; a species that is unlikely to be included as it is energetically unfavourable (Equation 3). Describes a relationship where the change in resistance is proportional to the concentration of the gas (in this example carbon monoxide, CO) and a sensitivity parameter A (the sensitivity parameter is constant for a given material at a given temperature) where R is the resistance after exposure to analyte gas and R_0 the baseline resistance (Equation 4):

$$\frac{1}{2}O_2 \underset{k^-4}{\overset{k_4}{\rightleftharpoons}} O^{2-} + 2P^+ \tag{3}$$

$$R/R_0 = 1 + A[CO] \tag{4}$$

Instead, Naisbitt *et al.* propose that Equation (1) is more likely, but to account for non-linear responses, there must be other factors influencing the response. First, the assumption is made that the only parts of the material that exhibit a response to the target gas, are the areas where the gas can reside and interact at the surface.

Figure 2. Demonstrating the structure of the materials, and the positions of the surface, bulk and particle boundary. Figure adapted with permission from Naisbitt *et al.* [13].

The model assumes the gas sensitivities of the surface and particle boundary are the same.

Thus, the material is split into three regions (Figure 2): (i) the surface, (ii) the bulk (inaccessible to the target gas), and (iii) the neck or particle boundary (below this boundary, the material is no longer defined as a surface). The distance between the surface and the particle boundary is called the Debye length; the distance at which charge separation can occur. The Equation for the response in this model is found to be Equation (5):

$$G_T = \gamma PB(1 + A[CO]) + 1/[(1/\gamma_B) + (1/\gamma S(1+A[CO]) \tag{5}$$

where G_T is the response ($G_T = R_T/R_{T,0}$), R_T is the total sensor resistance $R_{T,0}$ is the baseline resistance in clean, dry air and each $\gamma x = R_{x,0}/R_{T,0}$ gives (x denotes particle boundary, PB; bulk, B; or surface, S. So, γ is the ratio of the baseline of x to the total baseline of sensor resistance [7].
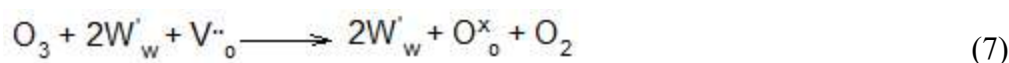
This work shows that the response time is directly related to the grain size and the size of the particle boundary in the material. The response model is different for n-type and p-type semiconductors. In forming the baseline resistance, oxygen is adsorbed on to the surface and abstracts electrons from the material; hence, this process will determine R_0. The resistivity of the p-type decreases relative to the bulk, and will increase for the n-type. The relative contributions from the three resistors in the model then differ. For very small grain sizes, the grain can be considered to contain no bulk area at all (so the whole grain is considered to contribute to the surface area) in this instance, the simpler model and Equation (4) is an adequate model for the response. If one considers the other extreme, where the grains are so large the contribution to the resistance or conductivity is negligible, the surface can be deemed to have a constant resistance. This model is expected to be generally applicable to both p and n-type sensors.

1.3. Sensor Response Disruption

The presence of other gases in the sensor headspace is important. The measurement of conductivity should ideally be only for the target analyte. If a contribution to the charge carrier concentration (whether this be an increase or decrease) comes from another gas, the sensor reading will be inaccurate, providing a false measurement. Some of the important disrupting gases are listed below.

1.3.1. Ozone

Oliver *et al.* showed that when the concentration of oxygen vacancies is high, the concentration of electrons is high on the surface [14] (5). This would elevate conductivity (for n-type material), but upon the introduction of ozone on the surface it is reduced, filling the vacancies (considered as negative holes) and lowering the conductivity (6). (Equations 6 and 7 in Kröger-Vink notation) [6].

$$W'_w \rightleftharpoons W^x_w + e^- \tag{6}$$

$$O_3 + 2W'_w + V^{\cdot\cdot}_o \longrightarrow 2W'_w + O^x_o + O_2 \tag{7}$$

If ozone is present in significant concentrations, the response of the material will be altered, leading to misleading figures as to the presence or concentration of the target gas.

1.3.2. Water

Water is thought to interact with the metal oxide, altering the conductivity of the film [15]. Water molecules form hydroxyl (OH^-) ions on the surface, directly introducing electrons that increase the conductivity of an n-type sensor (having little affect on a p-type sensor). The remaining hydrogen atoms react with the surface oxygen atoms, forming negative holes and increasing conductivity. Work by Korotcenkov *et al.* [16] investigated the effect of humidity on the response of a SnO_2 film, with the film demonstrating a decreased response time and larger responses in the presence of water. The authors suggest that the effect of water should be taken in to account when detecting reducing gases.

1.3.3. Volatile Organic Compounds

Research has demonstrated the indiscriminate response of SnO_2 films to varying hydrocarbons. Wang *et al.* [17] demonstrated that a metal oxide semiconductor sensor responds to methyl, ethyl, isopropyl and butyl alcohol. Indium tin oxide has been shown to respond to methanol, ethanol, butanol, and acetone by Vaishanv *et al.* [18]. Selectivity and control of sensor response is a major challenge in gas sensing using metal oxide semiconductor devices; trace levels of volatile organic compounds are present in virtually all environments.

1.4. Factors Influencing Sensor Design

Many factors must be addressed when designing a new metal oxide semiconductor gas sensor; such as the material's sensitivity and specificity to the gas in question or if the sensitivity of the material is appropriate for the application. The same gas sensor may not be appropriate in two different environments: a carbon dioxide sensor for the inside of a car exhaust should be designed for high concentrations, whereas one car cabin air quality should be far more sensitive to carbon dioxide at lower concentrations. The sensor would not be accurate enough to register concentration changes of 10 ppm if its sensitive range is 1,000–10,000 ppm. The surrounding pollutant gases will also affect the sensor gas response. As mentioned above (Section 1.3), certain gases will change the charge carrier concentration despite them not being the target analyte. A sensor in a photocopying room for example, might show unexpected results because the concentration of ozone is elevated; the ozone gas may interact with the film, nullifying or increasing a response. In this case, selecting a material that does not respond to ozone, altering the surface of the film or employing a suitable external filter to inhibit ozone interacting with the surface is necessary.
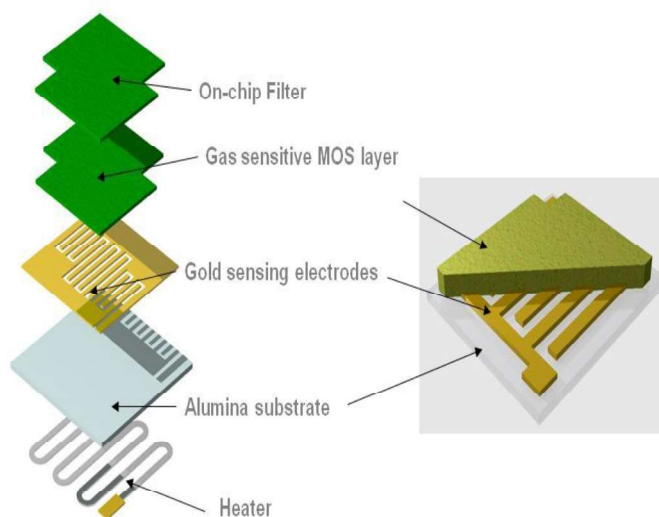
1.5. Techniques for Sensor Fabrication

Many fabrication methods have been used in the production of metal oxide semiconductor sensors. Factors that must be considered when selecting the production technique include; expense (if the films are expensive, the demand will be low and will have only limited applications), purity, porosity (if the material is highly porous, the surface area available to the gas for interaction will be far higher, giving a higher sensitivity), reliability and reproducibility [1]. Common techniques for making the metal

oxide films for gas sensors are mainly chemical vapour deposition (CVD), screen-printing of ceramic powders, sol-gel techniques and physical vapour deposition (PVD).

1.5.1. Screen Printing

Screen-printing is widely used in industry and the most widely used method for producing metal oxide semiconductor gas sensors commercially [8,18]. Screen-printing involves pushing an ink through a porous layer or mesh, which is suitably masked to produce the required layout on the substrate. The ink essentially contains the material to be deposited, dispersed in a viscous vehicle and is printed on of the substrate. Once the ink is has been deposited, the print can be heated to remove the vehicle, leaving a solid material on the specific target area. Figure 3 indicates the general form of commercial metal oxide semiconductor gas sensors.

Figure 3. Demonstrating the production of a gas sensitive film on a sensor substrate (diagram courtesy of Capteur Sensors and Analysers).
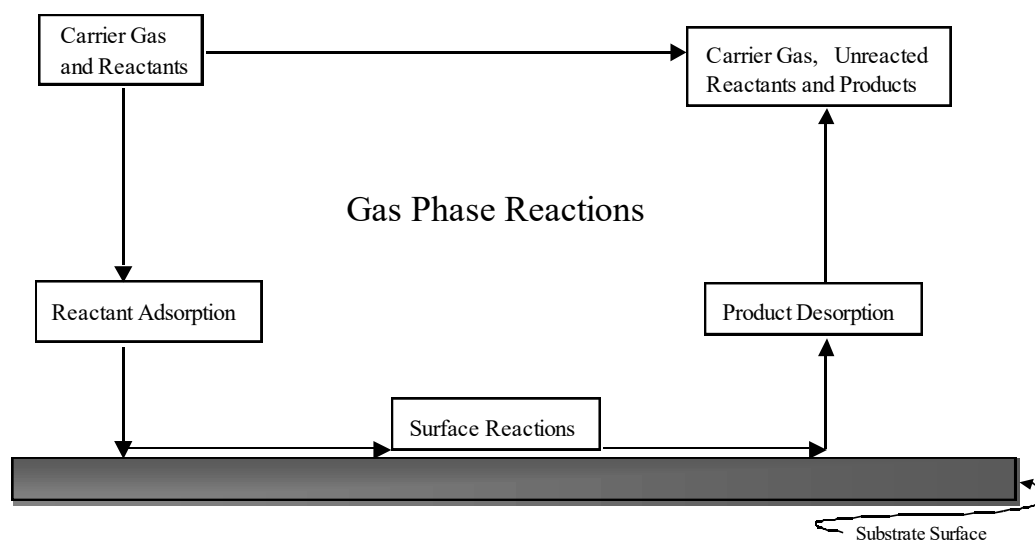

1.5.2. Chemical Vapour Deposition (CVD)

In CVD [19], a heated substrate is exposed to a precursor or controlled mixture of precursors in the vapour phase. The vapour(s) then react or decompose on the heated substrate forming a film of the desired material (Figure 4). Examples of different CVD techniques include atmospheric pressure CVD (APCVD), aerosol assisted CVD (AACVD); where non-volatile precursors have to be made in to an aerosol before deposition [20,21], or rapid thermal CVD where the substrate is heated, not the surroundings, avoiding unwanted reactions when the precursors are in the air. CVD gives control over important aspects of gas sensing materials; properties such as porosity, grain size and thickness can all be well controlled using CVD [3]. The speed of film growth is an advantage of the technique, with a rate of up to 1 μm a minute for processes that occur at atmospheric pressure. The problem of reactions in the gas phase in CVD can be addressed by reducing precursor concentration, though in doing so, the film growth rate is also reduced. Suitable precursors can also be an issue in CVD. Precursors must be

volatile enough in order to allow successful delivery to the heated substrate, but gas phase reaction and decomposition must be minimal, while having a structure that is thermodynamically able to decompose on the substrate giving the desired product is an area of significant research in producing any viable film.

Figure 4. A basic outline of the CVD method, depositing a film on to the substrate surface. Figure adapted with permission from [22].

APCVD has been used to deposit films of tungsten oxide for use as gas sensors by Binions *et al.* [23]. The gas sensors were shown to give a good response in the presence of ethanol. Williams *et al.* [24,25] have used CVD methodologies to produce films of WO_3 and chromium titanium oxide. This work demonstrated that the desirable high porosity of the gas sensitive film is obtainable via CVD routes. The suitability for the material as a gas sensor was not tested, but the author suggested the properties might be suitable for gas sensing.
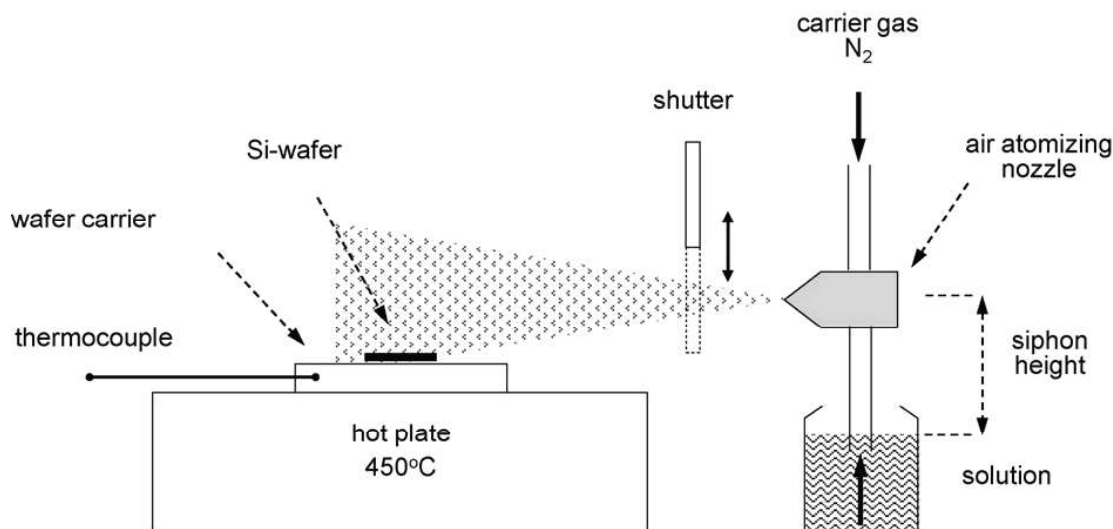
Blackman *et al.* [26-28] have used AACVD to produce high surface area, nanostructured tungsten oxide films with various precursors, with their gas sensing properties investigated. Choy [29] observes that AACVD is a useful technique when forming oxides and the aerosol is readily surrounded by oxygen, for larger scale applications, it could be favoured as it is a relatively low-cost technique. The area of AACVD is promising, but in industry it is proving difficult to produce a repeatable and controlled aerosol. A solution has not been found to tackle this problem. While the advantageous capabilities that this process has in producing good films has been demonstrated in the lab, the process has yet to successfully adapted by industry.

1.5.3. Spray Pyrolysis

Spray pyrolysis (Figure 5) is a technique where the reactants for the film are sprayed on to the target substrate. The deposited droplets then react on the surface when the substrate is heated, forming the desired film [30].

Figure 5. Demonstrating the spray pyrolysis technique for depositing thin films. Figure adapted with permission from Tischner *et al.* [30].
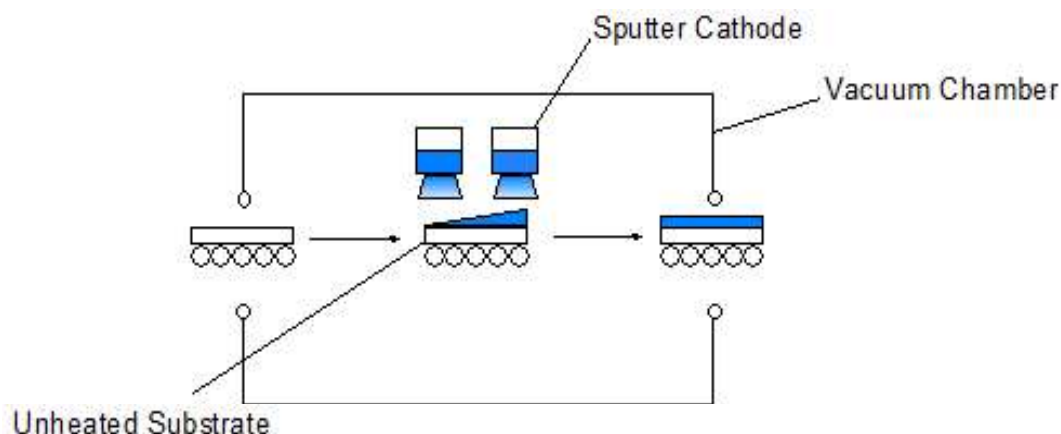

1.5.4. Sol-Gel

Sol-gel has been utilised for making gas sensitive films [14,31,32]. A recent report by Khun *et al.* uses the sol-gel method to synthesise SnO_2 particles, which then demonstrated a response in the presence of Ammonia. The sol-gel process involves the formation of a solution (sol)—a colloidal suspension of solid particles. The sol can then undergo gelation (gel—where cross linking between particles occurs), this can give new materials with other properties. In the case of ceramic film formation, the sol then undergoes evaporation, giving a highly porous xerogel film. Upon heating, the film then forms a dense ceramic glass on the surface.

1.5.5. Physical Vapour Deposition (PVD)

In PVD techniques (Figure 6) the material to be deposited is put into the gas phase by either evaporation through heating or by sputtering (bombardment of the material by ions) [33,34]. A reactive gas is introduced, where the gas atoms react with the metal vapour, forming a compound, which is then deposited on the substrate, giving a process where there is control over the overall property of the coating. The resultant film is well bound to the substrate. Michel *et al.* used magnetron sputtering to produce SnO_2 films [35]. The films were shown to have a level of conductivity, and upon exposure to hydrogen, the conductivity was shown to increase. Gupta *et al.* [36] produced a film of tin oxide by magnetron sputtering that demonstrated sensitivity to liquid petroleum gas. PVD is performed under vacuum; on large scale this can be an expensive technique. Growth rates, around 10 nm an hour makes this technique less suitable for high throughput for industrial applications.

Figure 6. Schematic of the PVD process, adapted with permission from Kanu *et al.* [19].

1.5.6. Drop Coating

Drop coating is a process by where a paste is made of the desired metal oxide powder and a suitable solvent; the paste is then deposited onto a substrate surface (in this case a gas sensor substrate) usually by controlled injection using a pipette. The deposited layer is subsequently fired to remove the solvent and attempt to improve adherence to the substrate [37]. The composition of the paste and nature of the dropping has a large influence on the film microstructure and subsequent sensor performance [38].

1.5.7. Comparison of Synthetic Techniques

The advantages and disadvantages of each synthetic technique for the production of metal oxide semiconductor gas sensors will be discussed. Physical vapour deposition techniques require vacuum or reduced pressure conditions, which are time-consuming to achieve and maintain, and expensive evaporation/sputtering/ablation equipment, which increases production costs. Therefore, economic factors restrict the commercial applications of PVD. However, this does allow for the more efficient use of precursors and facilitates the production of ultra thin films, in comparison to CVD. PVD may operate at lower temperatures; hence, is compatible with a variety of substrates. Given that no chemical reaction takes place in PVD, as opposed to CVD, careful precursor selection is not a main concern. However, the purity of the target is required to deposit non-contaminated thin films. A variety of target can be incorporated into the system without difficulty, developing multilayer arrays.

Sol-gel methods are straightforward to operate, but the time required to establish the sol is important for obtaining the desired product, thus can be a slow multi-step process. Full coverage of the substrate with moderately even thickness can be achieved (which can be tricky to control over larger substrates), by using readily available precursors, although these are often expensive. Dopants may be easily introduced and the sol-gel process has low processing temperatures.

CVD is a non-line-of-sight process (unlike PVD) with high deposition rates at relatively low temperatures, thus depositing films with good conformal coverage and enables the synthesis of pure and uniform thin films, which generally exhibit good adhesion. CVD produces dense films which is a disadvantage for gas sensors as the contribution from the bulk resistance is substantially increased