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Ứng dụng của công nghệ lắng đọng lớp nguyên tử trong cảm biến khí

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TÓM TẮT

Lắng đọng lớp nguyên tử (ALD) là công nghệ chế tạo vật liệu tiên tiến được ứng dụng rộng rãi trong nhiều lĩnh vực khác nhau. Nhờ vào tính chất tự bão hòa của các phản ứng trên bề mặt đế, ALD cho phép lắng đọng vật liệu với độ đồng đều cao trên mọi bề mặt và khả năng điều khiển chính xác kích thước của vật liệu ở mức độ nguyên tử. Do đó, ALD thường được dùng để lắng đọng các màng siêu mỏng hoặc các hạt nano trên bề mặt của các cấu trúc nano dị thể ứng dụng trong cảm biến khí nhằm làm tăng cường các tính chất điện và tính chất nhạy khí của vật liệu. Đặc biệt, trong thời gian gần đây, một số nghiên cứu cho thấy các vật liệu nhạy khí có độ nhạy và độ lặp lại chưa từng có có thể đạt được bằng cách kết hợp các quy trình ALD của các vật liệu khác nhau. Điều này cho thấy tiềm năng lớn của công nghệ ALD trong lĩnh vực cảm biến khí. Trong bài báo tổng quan này, chúng tôi trình bày tóm tắt những ứng dụng gần đây của ALD trong lĩnh vực cảm biến khí. Trong đó, chúng tôi tập trung vào hai ứng dụng chính của công nghệ ALD là biến tính bề mặt của các cấu trúc nano dị thể và chế tạo các vật liệu cảm biến tiên tiến.

Từ khóa: *Lắng đọng lớp nguyên tử, cảm biến khí, vật liệu màng mỏng, vật liệu hạt nano, vật liệu đơn nguyên tử.*

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Recent advances in atomic layer deposition of nanostructured materials for gas sensors

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ABSTRACT

Atomic layer deposition (ALD) has been widely used in the field of gas sensors thanks to the advantages of a non-line-of-sight technique that allows for conformal and uniform coating on virtually any type of substrates, and the capability of depositing various materials in a highly controlled manner. ALD is mainly applied for surface modification using ultrathin films or nanoparticles to fabricate heterostructures, which can drastically change the electronic transport properties and improve the performance of the sensing materials. Recently, ALD has been utilized to fabricate "all-ALD sensing materials", which exhibit unprecedented performance and outstanding reproducibility. This overall review summarizes recent advances in the fabrication of sensing materials for gas sensors by ALD, with focuses on two main applications: ALD for surface modification of sensing materials and ALD for fabrication of sensing materials.

Keywords: *Atomic layer deposition, gas sensors, ultrathin films, nanoparticles, single atoms.*

1. INTRODUCTION

Gas sensors have been popularly used to monitor air pollution. Nowadays, they also appear in most of high buildings, smart homes, and industrial manufacturing processes to detect gas leakage that helps prevent accidents and avoid equipment malfunction. In some emerging areas such as healthcare, gas sensors are used in exhaled breath diagnosis or to provide a correct gas mixture for the sake of safety and health of patients. Hence, it is no doubt that gas sensors have become an indispensable part of our daily life.[1–3]

Gas sensors can be classified into various types based on their sensing materials, such as semiconductor metal oxide (SMO) sensors, polymer sensors, carbon nanotube sensors, or based on their sensing principle, such as resistive sensors, electrochemical sensors, thermal conductivity sensors, acoustic sensors, and optical sensors.[4,5] Among these types, gas sensors using SMOs as sensing materials are most popularly used due to their high stability, low cost, and especially their chemiresistant behavior that represents a change in electrical resistance in response to the change in surrounding chemical environment.[4] Among the SMOs, SnO_2, ZnO, TiO_2, and NiO are most used. During the past decades, various nanostructures of SMOs have been developed, including nanowires, nanorods, nanotubes or 3D architectures (Figure 1), which exhibit superior performance as the sensing materials in chemiresistive sensors to achieve high sensitivity and selectivity.

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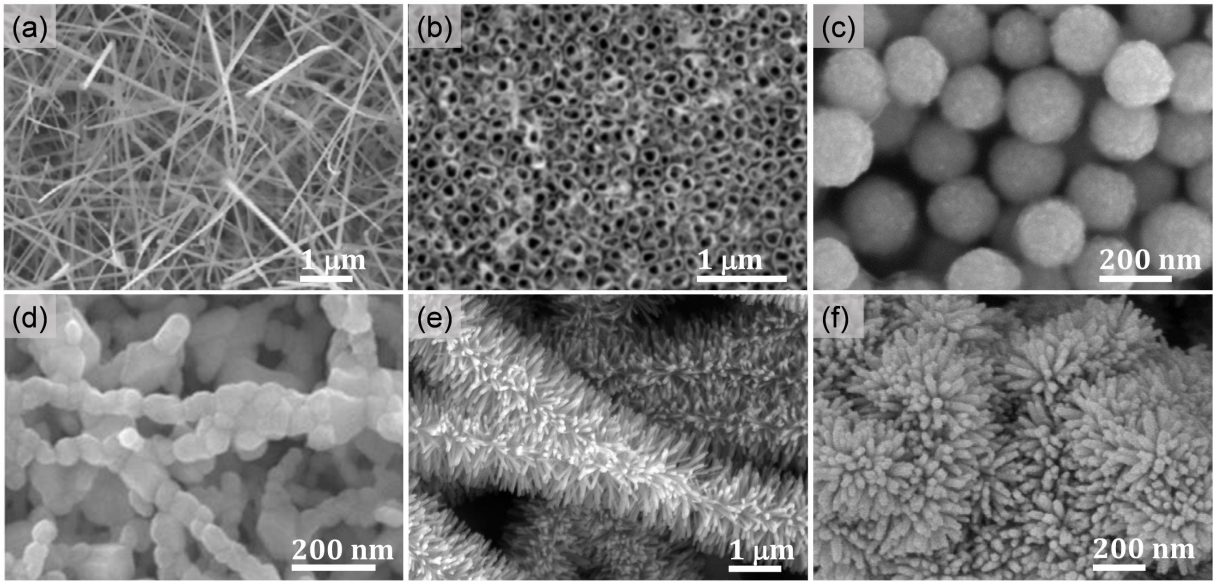

Figure 1. Several typical nanostructured SMOs used as sensing materials for gas sensors: (a) SnO_2 NWs,[6] (b) TiO_2 nanotubes,[7] (c) In_2O_3 nanospheres,[8] (d) WO_3 nanowires,[9] (e) ZnO 3D hierarchical structure,[10] and (f) SnO_2 3D nanoflowers.[11]

The advantages of using nanostructured SMOs as sensing materials rely firstly on their facile synthesis techniques. Most of nanostructures can be achieved by wet-chemistry methods, such as solvothermal and hydrothermal. Chemical vapor deposition is often used to grow high-quality materials (e.g., better crystallinity, lower impurity) due to the higher growth temperatures and the absence of solvent usage. Secondly, nanostructured SMOs allow for tuning the material properties by tailoring their shape and size, which can be obtained by adjusting the synthesis conditions, such as temperature, reaction time, precursor concentration or even pH of the solution. Thirdly, SMO nanostructures provide high specific surface area (SSA) for the adsorption of gaseous species, which is directly proportional to the sensitivity of the sensors. The high SSA of SMO nanostructures also allows for a higher loading of functionalized materials on their surface, with is currently a key technique for improving sensor performance. Hence, nanostructured SMOs have been the most attractive materials for gas sensors. Nevertheless, nanostructured SMOs synthesized by wet-chemistry processes are commonly in form of powders, which are usually transferred onto pre-patterned electrodes by using methods like screen-printing, dip-coating, and drop-coating to realize a sensor device, which is analogous to the process described in Figure 2A. This well-established fabrication process is quite effective and low-cost; however, it suffers from the lack of control in terms of uniformity and reproducibility of the sensing layer. On-chip fabrication of sensing materials, in which the sensing materials are selectively grown on top of the pre-patterned electrodes (Figure 2B), has been developed to replace the dip-/drop-coating methods, which significantly improves the electrical contacts between the sensing materials and the metal electrodes. However, it does not improve much uniformity and reproducibility of the fabrication process. High-precision sensing layer technology is of great significance for the reliable production of sensors and sensor arrays. In this regard, atomic layer deposition (ALD) has emerged as an ideal technology for depositing sensing materials.

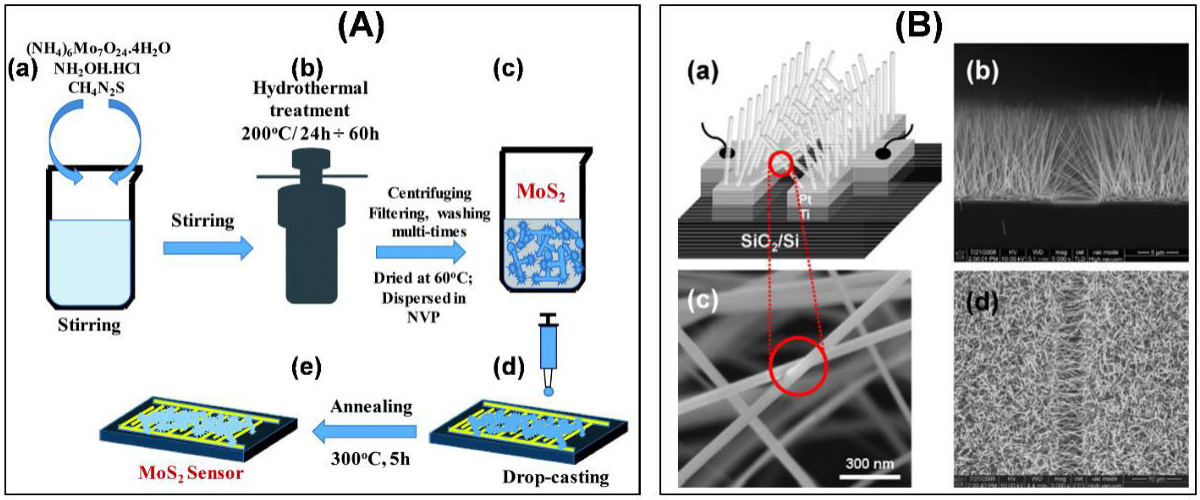

Figure 2. (A) Typical steps in a fabrication process of gas sensors employing sensing materials synthesized by hydrothermal method:[12] (a) mixing precursors and stirring, (b) hydrothermal treatment, (c) collecting and washing the solid product, (d) drop-coating of sensing materials onto pre-patterned electrodes, and (e) thermal annealing; (B) On-chip growth of ZnO nanowires:[13] (a) a schematic drawing describing the selective growth of ZnO, (b)-(d) SEM images of the ZnO nanowires taken in the area between the two Pt electrodes ((b) – cross sectional view and (d) – top view).

2. ATOMIC LAYER DEPOSITION

Atomic layer deposition (ALD) is a gas-phase deposition technique, which is a variant of chemical vapor deposition (CVD).[14] However, ALD can be carried out significantly lower temperatures, which are typically below 400 °C. In CVD, precursors are supplied continuously and co-exist in space and time above the substrate; however, in ALD, precursors are introduced in pulses sequentially and separately, and they are repeated in cycles.[15] A typical ALD cycle consists of 4 sequential pulses: (1) a pulse of the first precursor (i.e., precursor exposure), (2) a pulse of inert gas to evacuate the reaction by-products and unused precursor (i.e., purge), (3) a pulse of the second precursor or co-reactant, and (4) a pulse of inert gas to evacuate the reaction by-products and unused precursor. An animation representing a cycle of Al_2O_3 ALD using trimethylaluminum (TMA – precursor A) and H_2O (precursor B) is given in Figure 3. It is important to note that in ALD, the functional groups on the initial substrate surface are very important, which initiate the chemical reactions (i.e., chemisorption) with the gas molecules of precursor A when they are introduced to the reactor. These functional groups are commonly created by surface pre-treatment prior to the deposition. When TMA molecules are introduced into the reactor (step 1), they react with the functional groups (i.e., −OH) via the ligand-exchange reactions:[14]

$$-OH_{(surface)} + Al(CH_3)_{3(vapor)} \rightarrow -O-Al(CH_3)_{2(surface)} + CH_{4(gas)} \quad (1)$$

After all the −OH groups are consumed, the reactions reach a saturation (self-limiting), resulting in at most 1 monolayer containing Al atoms on the surface. The exceeding (i.e., unused) molecules and the by-products (i.e., CH_4 gas) are then evacuated by a purge of inert gas (step 2). In the next step, when H_2O is introduced into the reactor, the reactions between H_2O molecules and the newly formed ligands on the surface proceed as:

$$-O-Al(CH_3)_{2(surface)} + HOH_{(vapor)} \rightarrow -O-Al(OH)_{2(surface)} + CH_{4(gas)} \quad (2)$$

Similarly, when all the ligands have reacted with H_2O, the reactions stop, forming at most 1 monolayer containing O atoms, and

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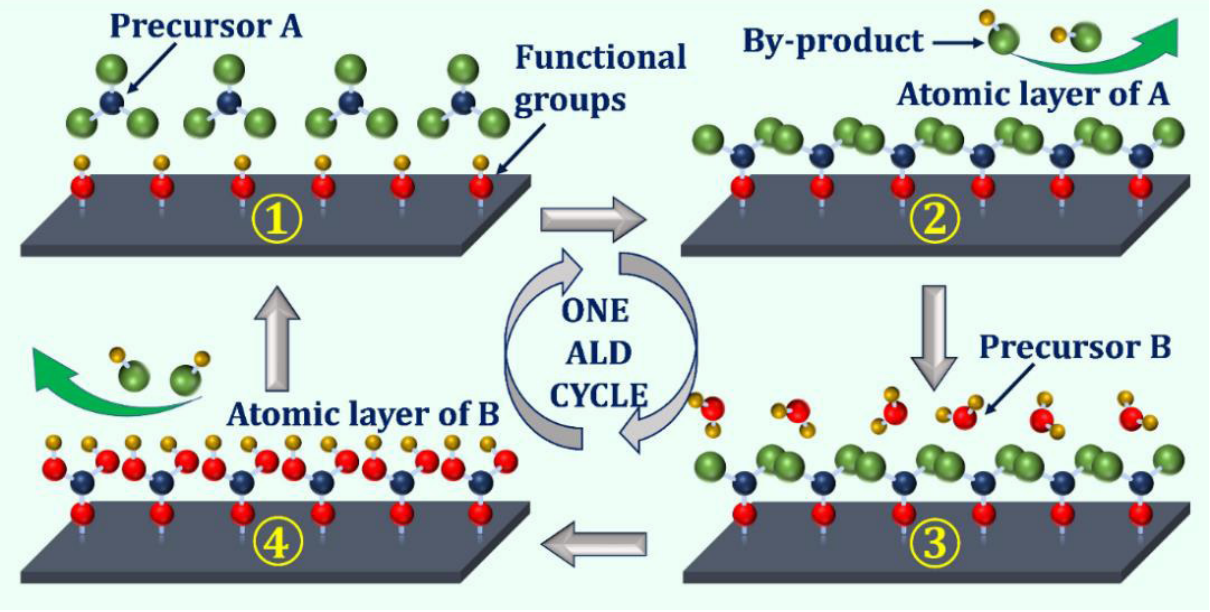

Figure 3. A typical ALD cycle consisting of 4 pulses: (1) precursor A, (2) inert gas, (3) precursor B, and (4) purge.

the surface is now terminated by −OH groups, which are necessary for the reactions with TMA molecules in the next cycles. Reaction (1) and reaction (2) are commonly known as the two "half-reactions" in an ALD cycle. Typically, the growth rate in ALD is in the range of a few angstroms per cycle. Hence, by controlling the number of cycles, the film thickness and the amount of deposited material can be controlled at the atomic level. This is a unique property of ALD, which allows for uniform and conformal coating on various types of substrates with different geometries, such as flat substrates, high aspect ratio structures, 2D materials, porous structures, nanoparticles, and nanowires (Figure 4).

Thanks to the advantages of a solvent-free method with excellent controllability, ALD has been applied in many fields, including electronic and photovoltaic devices,[21,22] catalysis,[23] and energy storage and conversion materials.[24–26] Recently, ALD has been also applied in the field of gas sensors, which is used to deposit ultrathin films of SMOs such as SnO_2, ZnO and TiO_2, as well as nanoclusters of noble metals such as Pt, Pd, and Ni, as presented concisely in a recent review by Marichy and Pinna.[27] The applications of ALD in gas sensors can be divided into two groups: ALD for surface modification of sensing materials and ALD for fabrication of sensing materials.

2.1. ALD for surface modification of sensing materials

Surface modification is a common technique to tailor the properties of materials by coupling them with other materials. Particularly in gas sensors, to improve the selectivity and sensitivity of the sensing layers, they are usually coated with ultrathin films of SMOs or with nanoparticles of noble metals the create various types of heterostructures, such as n−n and p−n heterojunctions.[28] The most investigated heterostructure in gas sensors is the core/shell structure. Due to their different electronic band structure, heterojunctions can drastically change the electronic transport of carriers and improve sensing properties compared to their single components. For example, SnO_2 nanostructures are excellent sensing materials that have been used to detect various types of gases, both reducing and oxidizing gases.[29] However, coating a thin layer of ZnO on SnO_2 nanofibers to form an n-ZnO/n-SnO_2 heterojunction could significantly alter the sensing properties of SnO_2:

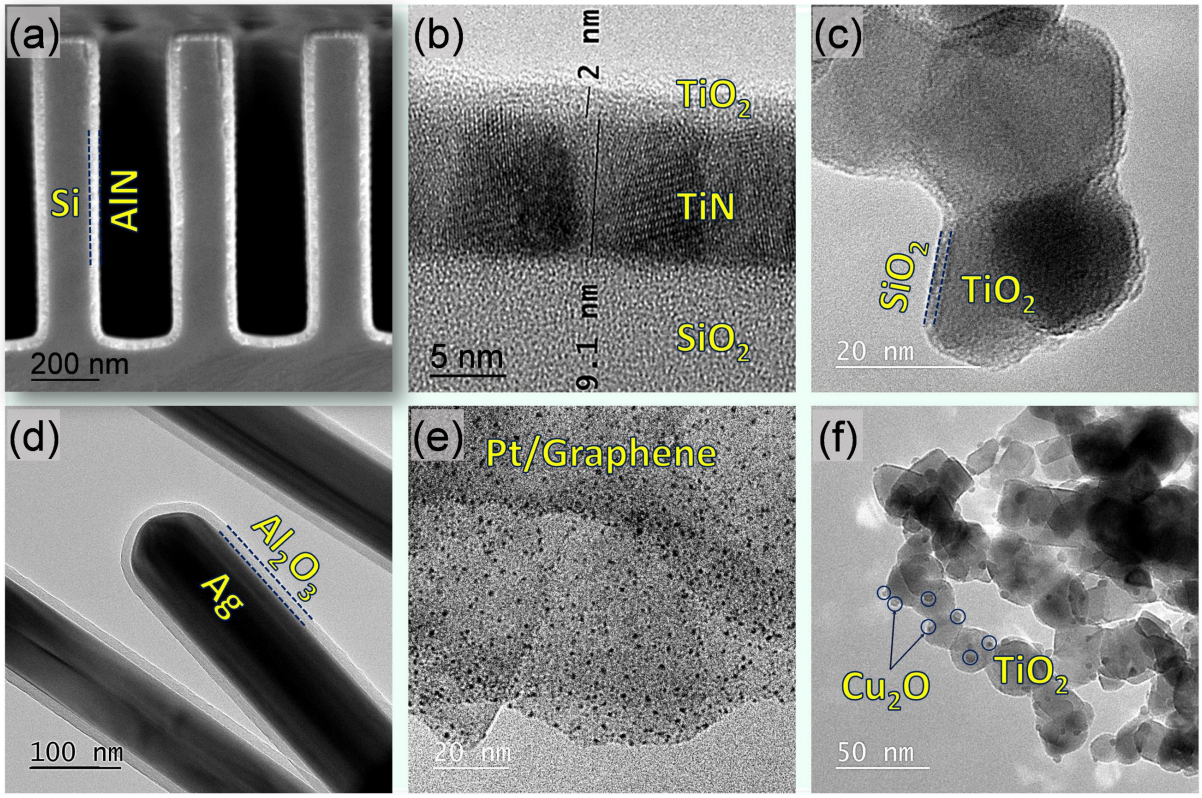

Figure 4. Examples of the uniformity of thin films and nanoclusters deposited by ALD: (a) AlN thin film on Si substrate with trenches,[16] (b) TiN thin film on SiO_2,[17] (c) SiO_2 thin film on TiO_2 nanoparticles,[18] (d) Al_2O_3 thin film on Ag nanorods, (e) Pt nanoclusters on graphene,[19] and (f) Cu_2O nanoclusters on TiO_2 nanoparticles.[20]

the core-shell structure is highly effective in detecting gases only and weakens the sensitivity toward oxidizing gases.[30] A p−n heterostructure based on p-CuO/n-ZnO core/shell nanofibers exhibited superior performance with a prominent enhancement of sensing ability compared to the bare ZnO nanofibers, allowing for detecting reducing gas CO at extremely low concentrations, i.e., down to 0.1 ppm.[31] Many other core/shell structures of MSOs have been utilized in gas sensors, such as MoO_3–TiO_2,[32] CeO_2–TiO_2,[33] In_2O_3–ZnO,[34] Fe_2O_3–ZnO,[35] Ga_2O_3–SnO_2,[36] and Ga_2O_3–ZnO.[37] In all cases, the thickness of the shell layer plays a pivotal role in the performance of sensing layer. Particularly, when the shell thickness is in the range of the Debye length of the shell material, the highest performance is achieved. For example, the n-ZnO/n-SnO_2 core/shell structure exhibited the highest sensitivity for the ZnO thickness of 20 nm (Figure 5A),[30] whereas an optimum shell layer of 16 nm was found for the p-CuO/n-ZnO core/shell structure (Figure 5B),[31] both of which are in the Debye length range of the shell layers. These examples indicate that achieving heterostructured gas sensors with desired properties and optimum performance requires a precise thickness of the shell layer. Hence, ALD has been widely used to deposit various SMO thin films to realize different heterostructures for gas sensors, as presented in Table 1.

The coupling of SMOs with nanoparticles of noble metals and transition metals such as Pt,[38] Pd,[39] Ru,[40] Ag,[41] and Co[42] has been an effective method to improve the sensitivity, selectivity and response of gas sensors. The enhanced performance of the sensors due to the presence of the metal nanoparticles is attributed to two key factors: the catalytic activity of the metals (chemistry aspect) and the formation of Schottky contacts between the metal and the SMO (physics aspect).[10] In the chemistry aspect, the high catalytic activity of the meal nanoparticles

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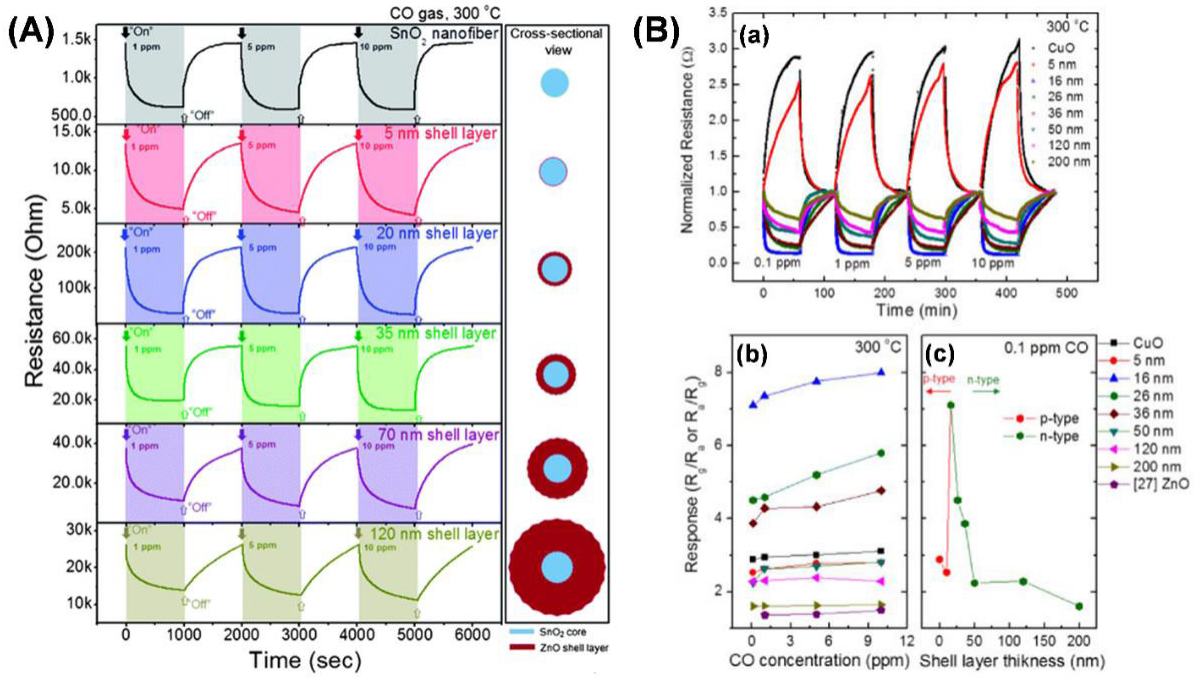

Figure 5. (A) Influence of the shell thickness on the response of sensors based on n-ZnO/n-SnO_2 core/shell structure;[30] (B) for p-CuO/n-ZnO core/shell structure with the shell thickness being varied in the range of 0–200 nm:[31] (a) Dynamic response curves, (b) responses at various CO concentrations, and (c) responses at 0.1 ppm CO.

promotes the adsorption of oxygen on the SMO surface, which enhances the extraction of electrons from the SMO to create ionic oxygen species. The enhanced extraction of electrons can cause a significant change in the SMO resistance, whereas the higher density of ionic oxygen species on the SMO surface provides more active sites for the interaction between the detected gas and the sensing layer. In the physics aspect, the presence of metal nanoparticles create Schottky junctions on the SMO surface in the vicinity of the nanoparticles.[64] This narrows the conducting channel, resulting in the increase in resistance. Both the chemistry and the physics aspects can bring a significant improvement of sensitivity, selectivity, and response of sensors. For example, Rh nanoparticles on SnO_2 nanofibers can act as effective adsorption sites to bind and dissociate oxygen molecules. This increases the adsorbed oxygen content, resulting in a thicker electron depletion layer and an increase resistance. Another example, the surface modification of ZnO hierarchical nanorods by Pt nanoparticles improved the selectivity of the sensor to methanol, increased its response approximately 19500 times and significantly lowered the operating temperature compared to the pristine ZnO.[10] In that case, the Pt nanoparticles not only enhanced the adsorption of O_2, but also promoted the dissociation of methanol molecules and facilitated the electron transfer from Pt to ZnO, which consequently caused an abnormal decrease of resistance of sensing layer when exposed to methanol. These are a few examples among numerous research on the advantages of surface modification of sensing materials by metal nanoparticles that have been reported in the literature. With the advantages of a non-line-of-sight technique that allows for conformal and uniform coating on all kinds of substrates, and the capability of depositing various pure metals in a highly controlled manner, ALD of metal nanoparticles has been recently applied for functionalize nanostructured metal oxides in gas sensors. Due to their high catalytic and sensing activities and well-developed ALD processes, Pt and Pd are most used. A few examples are given in Table 1.

Table 1. SMO thin films and noble metal nanoparticles grown by ALD for surface modification of nanostructured sensing materials.

Material (Shell)	Substrate (Core)	Shell thickness/ Cluster size (nm)	Junction type	Test gas	Ref.
ZnO	Graphene	0.5 – 10	n–n	HCHO, NO_2	43
	SnO_2 nanofibers	22 – 250	n–n	O_2, NO_2, CO	44
	SnO_2 nanorods	3.5 – 9.5	n–n	CO, NO_2; C_7H_8, C_6H_6	45
	TiO_2 nanorods	20	n–n	C_2H_5OH	46
	TiO_2 nanofibers	50 – 250	n–n	O_2	47
	WO_3 nanorods	15	n–n	NO_2	48
	In_2O_3 nanowires	10 – 53	n–n	C_2H_5OH	49
	CuO nanorods	9	n–p	NO_2	50
	CuO nanowires	5 – 110	n–p	C_6H_6	51
	CuO nanofibers	5 – 200	n–p	CO	31
SnO_2	Carbon nanotubes	1.5 – 15	n–p	NO_2	52
	CuO nanowires	0 – 31	n–p	HCHO	53
	TiO_2 nanotubes	4 – 16	n–n	NO_2	54
	Ga_2O_3 nanowires	2 – 15	n–n	C_2H_5OH, NH_3, CO, H_2	36
	WO_3 nanosheets	5 – 30	n–n	NH_3	55
	Nb_2O_5 nanorods	7 – 34	n–n	H_2S	56
TiO_2	ZnO nanorods	10	n–n	RH, NO_2	57
	Carbon nanotubes	1.5 – 15	n–p	O_2, NO_2	58
NiO	SnO_2 nanowires	2 – 82	p–n	H_2	59
	Carbon nanotubes	0.8 – 21.8	p–p	Acetone, C_2H_5OH	60
	Co_3O_4 nanoparticles		p–p	Trimethylamine	61
Cu_2O	SnO_2 nanowires	5 – 80	p–n	NO_2	62
CuO	SnO_2 nanowires	5 – 80	p–n	NO_2, C_7H_8, C_6H_6	51
SiO_2	SnO_2 nanowires	1.8 – 10.5		H_2	63
Pt	SnO_2 nanowires	4 – 8	Schottky	C_2H_5OH	64
	Al_2O_3/ZnO nanorods	3 – 5	Schottky	Acetylene	65
	MoS_2 nanoflakes	< 1	–	H_2	66
Pd	ZnO nanowires	10	Schottky	C_6H_6, C_7H_8, C_2H_5OH, CH_3COCH_3	67
Rh	ZnO nanoflowers	0.4 – 1.6	Schottky	Trimethylamine	68

2.2. ALD of sensing materials

In addition to the application in modifying the surface of SMO nanostructures, ALD has also been used to deposit thin films of SnO_2,[69–71] TiO_2,[72,73] and ZnO[74] as the sensing layers for gas sensors directly on top of substrates without the need of complex nanostructures. The studies on the sensing performance of these thin films also revealed the strong influence of film thickness on the sensitivity and response of the sensors. For example, Rosental et al.[69] investigated the sensing properties of ALD SnO_2 films toward CO gas and observed that the maximum performance was achieved for the layer with a thickness of 10 nm. This thickness is comparable to the Debye length of SnO_2. Du et al.[70] found that the sensor

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response changed drastically by varying the SnO_2 thickness in a very narrow range, i.e., 1.6–5.9 nm. The use of ALD not only provides precise control of the film thickness, but also tackles the uniformity and reproducibility issues that are commonly encountered in traditional sensor preparation techniques (i.e., drop-/dip-coating of sensing materials on prepatterned electrodes).

Up to date, ALD of shell layers, including SMO thin films and metal nanoparticles, for gas sensors has been widely utilized. However, this approach can only offer an improved performance of sensors, but it cannot solve the problems in the reproducible fabrication gas sensors due to it is still strongly dependent on the fabrication of the nanostructures (e.g., wet chemistry) and transfer them to the sensor electrodes (e.g., drop-/dip-coating). An "all ALD" or "ALD only" process in which all materials are deposited by ALD is highly desirable for taking full advantages of ALD: Precise control, uniform, and reproducible. This has just been realized very recently by Zhang et al,[75] who fabricated the sensors based on SnO_2 ultrathin films and Pt single atoms, both deposited by ALD (Figure 6A), and investigated their sensing performance to triethylamine (TEA) gas. The work is distinctive from existing research in developing sensing materials for advanced gas sensors, both in both fundamental mechanistic and technological aspects. For the first time, Pt single atoms were used to improve the sensing properties of SnO_2 ultrathin films with thicknesses in the range of a few nanometers, resulting in an exceptionally high sensitivity of 8.76 ppm^{-1} and an extremely low detection limit of 7 ppb. The sensors also exhibited excellent selectivity, low operating temperature, very fast response and recovery (Figure 6B), which are

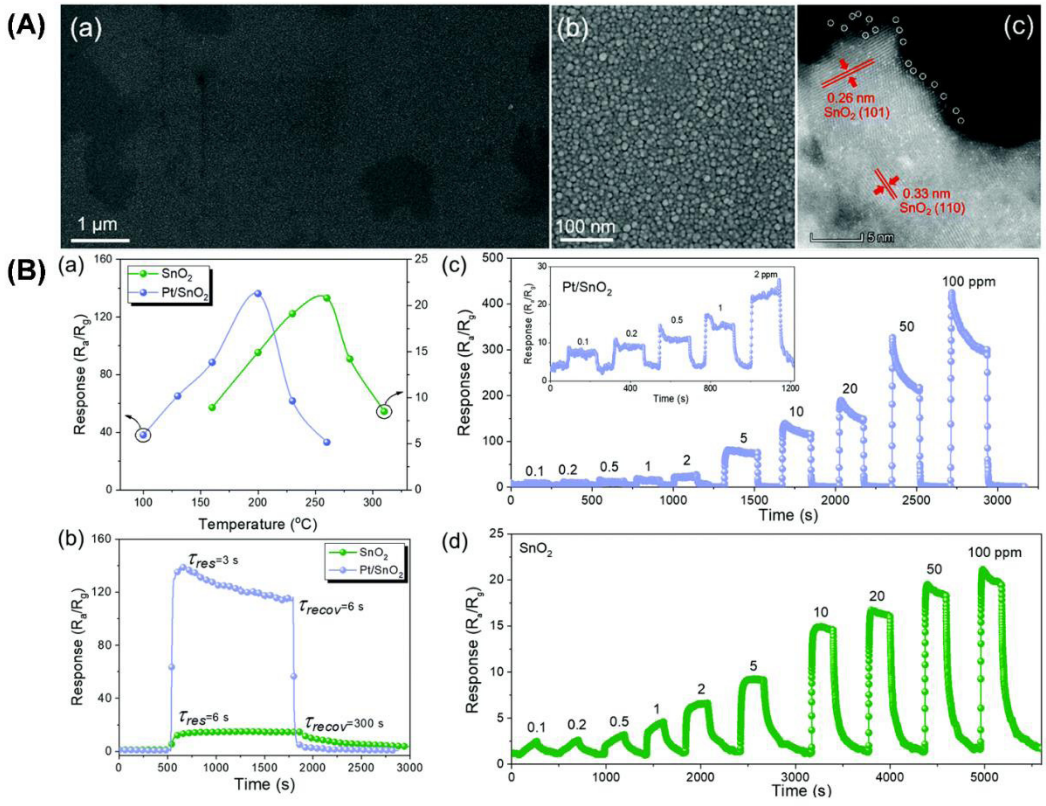

Figure 6. (A) Structural characterization of SnO_2 and Pt/SnO_2 thin films: (a & b) SEM images of a SnO_2 thin film, and (c) HAADF-STEM image showing the presence of Pt single atoms. (B) Sensing performance of the Pt/SnO_2 toward TEA vapor: (a) responses to 10 ppm TEA of SnO_2 and Pt/SnO_2 thin films (9 nm) at different temperatures; (b) dynamic transients of SnO_2 and Pt/SnO_2 thin films to 10 ppm TEA at 200 °C, and dynamic transients of (c) Pt/SnO_2 and (d) SnO_2 thin films to TEA concentrations in the range of 0.1–100 ppm at 200 °C.[75]

far beyond the results reported in the literature.[75] Most recently, an "all ALD" process has also been demonstrated by Zhuiykov et al. for the fabrication of heterostructures based on SnO_2 and In_2O_3 ultrathin films with a total thickness of below 10 nm at wafer scale.[76] Without the use of functionalized metal nanoparticles, the sensors based using SnO_2/In_2O_3 heterostructures also exhibited excellent sensitivity, high rate of gas detection, good selectivity and long-term stability. The sensitivity of S = 53 and limit of detection of ~1.0 ppm towards ethanol achieved by the ALD fabricated SnO_2/In_2O_3 heterostructures are the highest performance of the reported sensors based on SnO_2 and In_2O_3 composites prepared by various methods.[76] Hence, the excellent performance of the sensing materials prepared by an "all ALD" process in combination with the great advantages of ALD (precise control, high reproducibility, high uniformity and well-established large scale production) can pave the way for the scalable production of reliable and high performance thin film sensors.

3. CONCLUSIONS AND OUTLOOK

The versatility and precision offered by this ALD make it an ideal choice when developing novel sensing layers, as well as engineering complex nanostructures that further improve performance levels while providing additional perspectives into development processes related to these types of technologies. Hence, ALD has been widely applied in the fabrication of resistive gas sensor devices, where at least one step involves using this method. On the one hand, an effective surface modification method, ALD has been employed to deposit ultrathin films and nanoparticles of a wide range of materials on virtually any sophisticated nanostructures. This provides a feasible route to realize heterojunctions of sensing materials, which can drastically change the electronic transport properties and improve the sensing performance. On the other hand, ALD can be used to realize all-ALD-fabricated nanostructures. This approach not only allows for the fabrication of novel nanostructures with unprecedented sensing performance in the sensitivity, selectivity, and stability, but also assures the high reproducibility and reliability of the sensors, which are highly important for practical applications. Furthermore, its compatibility with integrated circuits makes it a cost-effective solution compared to other fabrication methods which can lead towards more widespread adoption in various industries such as automotive or medical applications where reliable detection systems are essential.

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