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A review of nanostructured thin films for gas sensing and corrosion protection

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Abstract: Thin film technology is getting huge attention across the world due to its wide applications. Deposition of thin films involves creation, transportation and condensation of target materials with thickness varying from few nanometers to several microns onto the substrate. This review will highlight thin film depositing techniques which consist of non-vacuum and vacuum based deposition method. Besides this, thin films and their applications in gas sensing and corrosion protection have also been discussed.

Keywords: thin films; semiconductor; gas senor; deposition; corrosion protection.

Introduction

Thin Film Technology

Thin film technology has progressed rapidly in the direction of thin film coating and also has been developed for the need of the industry. It serves a number of purposes for various uses, including electronics (flexible polymer light-emitting displays [1], optical coatings (anti-reflection coatings [2]), superconducting films (SQUID[3]), magnetic films (data storage [4]), environmental (smart window [5]), energy (solar cells [6-10]), heat prevention & corrosion resistance (gas turbine components [11,12]), and super hard coatings [13]. Thin film coating can be classified according to coating thickness. Usually, researchers have deposited films with thickness in the range of a few nanometers to 10 µm are considered thin-film coatings. The thin films can have different properties compared to bulk material [14-16]. Common processes in recent thin-film technology include vacuum based and non-vacuum based technology as shown in Figure 1.

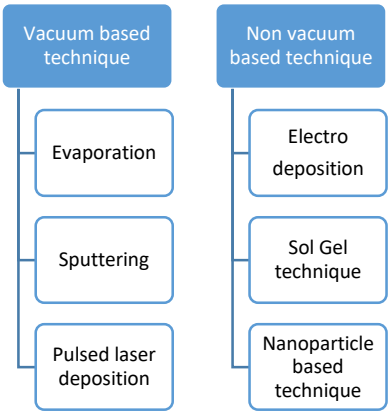

Figure1. Various thin film deposition techniques.

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Various Deposition Techniques

Various vacuum [17-20] and non-vacuum based techniques [21-24] have been used for depositing thin films by various researchers across the globe. Researchers are using these techniques for depositing thin films for different applications. These methods are briefly discussed below.

Vacuum Based Technique

Vacuum-based techniques have been the standard for high-quality semiconductor fabrication for a range of applications from microelectronics to photovoltaic cells. Here, evaporation, sputtering and pulsed laser deposition were selected as shown in Figure 1.

Evaporation

Evaporation is a well-known technique for depositing thin films for many applications. In this technique, the material is heated inside a high vacuum chamber. Low vapor pressure is sufficient enough to raise a vapor cloud inside the chamber and deposit on to the substrate. The basic thermal evaporation schematic is shown in Figure 2.

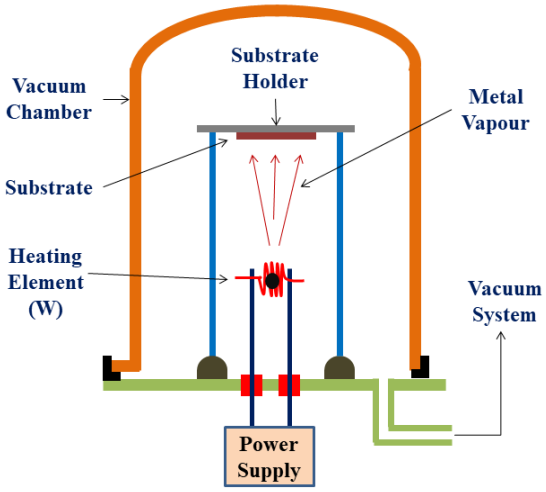


Figure 2. Schematic of evaporation technique

Memarian and co-workers deposited nanostructured CdS thin film using thermal evaporation and study the effect of temperature (25 to 250 °C) on film [25] in a vacuum of about $2X10^{-5}$ Torr. The resistivity values observed (3.11 to 2.2 X 10^4 Ω.cm) depend on the substrate temperature. Daniel and co-workers studied Cu_3SbS_3 thin films deposited by evaporation for solar energy harvesting application [26]. Jung and co-workers fabricated copper indium gallium selenide (CIGS) thin film solar cells using evaporation and study the effect of Ga content on properties of absorber material [27]. Steinmann and co-workers demonstrated tin sulfide solar cell with 3.88 % efficiency by using evaporation [28]. Xu and co-workers studied microstructure and properties of ZrC-SiC multi-phase coatings prepared by thermal evaporation where ZrC-SiC coatings have a multi-layered structure with low silicon (Si) content, and a single ZrC_x-SiC layer with high Si content [29].

Sputtering

Sputtering is a process whereby coating material is dislodged and ejected from the solid surface in the form of atoms/molecules due to the momentum exchange associated with surface bombardment by energetic particles. This phenomenon is known as sputtering, as shown in figure 3. McClanahan and co-workers have presented a historical review of sputter deposition [30]. DC (direct current) sputtering is used to deposit metallic films where RF (radio frequency) sputtering is to deposit insulating oxide films. Reactive sputtering is a process where the target is sputtered in the presence of a gas or a mixture of gasses (e.g. Ar + O_2) which reacts with the target material to form a coating of a different chemical compositions.

Singh and co-workers deposited petal type structure of Cu_2ZnSnS_4 (CZTS) using reactive sputtering [31]. Siol and other workers demonstrated reactive sputtering of In_2S_3 as an alternative contact layer for CZTS thin film solar cells from the single target in the presence of 98 % argon and 2 % H_2S gas mixture [32]. Gour and co-workers deposited CZTS thin film using DC sputtering and studied the effect of sodium on properties of deposited thin films [33]. In another study, CuIn and CuGa were deposited on a glass substrate using DC sputtering followed by post selenization for CIGS thin-film solar cell applications [34]. Gorjanc and other workers deposited indium tin oxide (ITO) thin film on a glass substrate using radio frequency (RF) sputtering at room temperature having transparency between 70-90 % in the visible range, and the sheet resistance was about 18 Ω.cm [35]. Choi and other workers studied the effect of oxygen concentration on properties of Zn(O,S) thin film deposited using RF sputtering [36]. Gour and other workers studied the effect of NaF on properties of the $Cu_2ZnSnSe_4$ thin film deposited using RF sputtering from in-house made single target for solar cell applications [37].

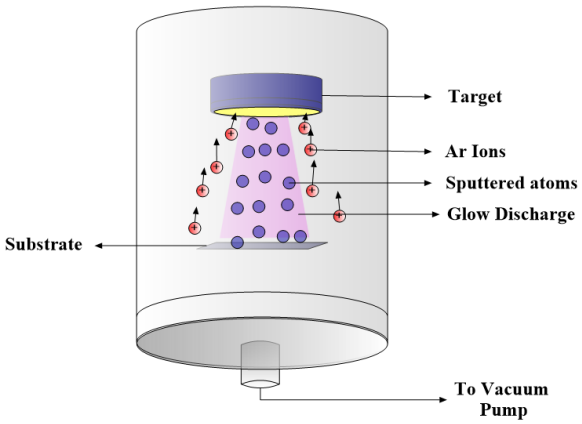


Figure 3. Schematic of the sputtering phenomenon.

In another study, $Cu_2ZnSn(S, Se)_4$ thin film based photodetector for visible range were fabricated using RF reactive sputtering [38]. Obeng and other workers deposited molybdenum sulfide (MoS_2) thin film using reactive sputtering [39]. Gour and other workers demonstrated rice-like nanostructured (rln) CZTS thin film based self-powered broadband photodetector deposited on a glass substrate using reactive sputtering [40]. Gour and other workers prepared DC magnetron-sputtered Zn(O, S) films on a quartz substrate and studied the effect of sulfurization temperature on optical, morphological, elemental and structural properties [41]. Gour and other workers studied the effect of Ag incorporation on properties of reactively sputtered CZTS thin film for solar cell and other optoelectronic device applications [42]. Huq and other workers deposited GaN thin film using RF sputtering and studied the effects of surface disorders and incorporate on the thin films characteristics [43]. Singh and other workers fabricated CZTS thin film solar cell having efficiency of 2.84 % using reactive sputtering on glass substrate [44]. Singh and other workers studied the effect of sodium on the performance of CZTS based photodetector for visible to NIR range [45].

Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) has been used to deposit high-quality thin films of materials. In this technique, high power laser pulses (about ~10^8 Wcm^{-2}) were used to strike to a material that is to be deposited onto the substrate. The melted, evaporated and ionized material from the surface of a target comes from the target in the form of plasma. The ablated material is collected on a suitably placed substrate upon which it condenses, and the thin film grows on to the substrate. Figure 4 shows the schematic of the pulsed laser deposition technique. Zhao and co-workers deposited ZnO thin film on a silicon substrate where film deposited in no-oxygen ambient at 500 °C used as a buffer layer for growth of ZnO thin films [46]. Zeng and co-workers studied substrate temperature dependent (300 to 700 °C) ZnO thin films prepared on titanium substrate using PLD for microwave, and medical applications [47].

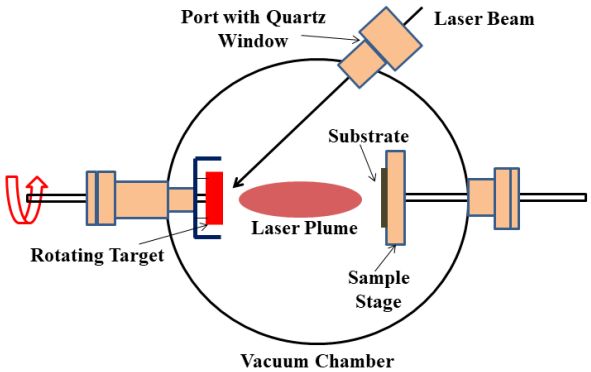


Figure 4. Schematic of pulsed laser deposition technique.

Han and co-workers deposited cascade structure of $Bi_2S_3/CuInS_2/TiO_2$ thin films using PLD technique for high photoelectrochemical performance for the direct fabrication of QD sensitized solar cells [48]. Yamaki and co-workers demonstrated epitaxial TiO_2 films sapphire substrate by using PLD for photocatalyst applications [49]. Kotani and co-workers studied compositional analysis of CZTS thin film deposited on soda lime glass substrate [50].

Non-Vacuum Based technique

Cost-effectiveness is the core of the development of any new technology. In this work, several non-vacuum methods such as electrodeposition, sol-gel, and nanoparticle-based technique have been chosen for the deposition of thin films based on various materials. These methods are briefly discussed below.

Electrodeposition

Electrodeposition is considered one of the low-cost methods for the production of semiconductor thin films. Electrodeposition, also well-known as electroplating, is the technique in which material deposited onto a conducting surface from a solution containing ionic species.

This deposition technique is mostly used to deposit thin films of material to the surface of an object to change its external properties such as to increase corrosion protection, increase abrasion resistance, improve decorative quality, or simply to deposit a layer which is part of a more complicated device. Schematic of electrodeposition is shown in figure 5. In this technique three electrodes are used which are working, reference, and counter (sometimes secondary) electrodes, respectively. The electrodes are connected to a potentiostat which is the instrument which controls the deposition process. These electrodes were kept within a container containing a liquid which has ionic species dissolved within it, such as copper ions dissolved in water. Rashid and co-workers deposited Cu_2ZnSnS_4 (CZTS) thin film grown on conducting glass substrate using a single step by using electrodeposition technique and studied the optical and structural properties[51]. Pawar and co-workers deposited Cu_2ZnSnS_4 thin films for solar cell application using electrodeposition technique on Mo coated glass and ITO glass substrate and studied structural, morphological, compositional, and optical properties [52]. Jiang and co-workers demonstrated co-electrodeposited Cu_2ZnSnS_4 thin film solar cell and Cu_2ZnSnS_4 solar cell-$BiVO_4$ tandem device for unbiased solar water splitting application [53]. Relekar and co-workers studied effect of electrodeposition potential on surface free energy and supercapacitance of MnO_2 Thin Films prepared by electrodeposition technique they observed specific capacitance (Cs) of MnO_2 thin films is 127 F/g for the deposition potential at 1.20 V/Ag/AgCl and films also show better stability for over 1000 cycles [54].

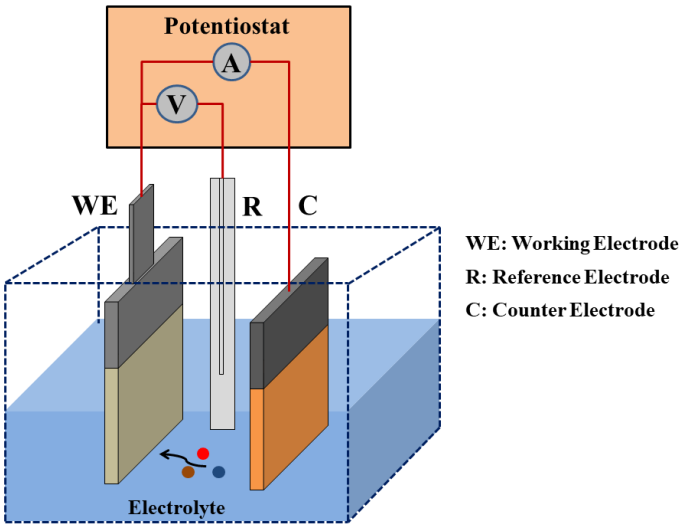


Figure 5. Schematic of the electrodeposition technique.

Premnath and co-workers deposited $Co_{1-x}Mo_xS$ thin films using electrodeposition technique on doped tin oxide (FTO) substrate which can be used as electrocatalysts for hydrogen evolution reaction (HER) in acid medium [55]. Thomas and co-workers deposited silicon/rare earth (Er, Tb) thin films on n-doped silicon (100) substrate using single step electrodeposition process and carried out compositional, optical and microscopic analysis for optoelectronic applications [56]. Zhang co-workers deposited nanocrystalline CoFe soft magnetic thin films using electrodeposition technique from citrate-stabilized baths [57]. Xia and co-workers deposited Ni-doped TiN thin films by jet electrodeposition and studied microstructural, corrosion properties and mechanical deformation response of deposited films using high-resolution transmission electron microscopy, X-ray diffraction, electrochemical workstation and triboindenter [58]. Altiokka co-workers deposited CdS thin films at various pH values using electrodeposition. Compact CdS films with good crystallinity [59] were obtained at pH value of 4 and 5. Jiang and co-workers deposited graphene-Sb_2Se_3 thin films as photoelectrode using electrodeposition for photoelectrochemical water splitting [60]. Thorat and co-workers deposited nanocrystalline Bi_2Te_3 thin films onto stainless steel substrates using electrodeposition technique for photoelectrochemical

application. The photoconversion efficiency and fill factor of photoelectrochemical (PEC) cell made by Bi_2Te_3 film were 0.0987 % and 0.3979 %, respectively [61]. Zhang and co-workers deposited thin NiFe hydroxide film as electrode for solar-to-chemical energy conversion [62]. Devi and co-workers deposited Fe–Ni–P thin films using electrodeposition and studied the effect of heat treatment on structural, optical and magnetic properties of deposited films [63]. Mahato and co-workers deposited cadmium selenide (CdSe) thin films on ITO coated glass substrates using electrodeposition technique and studied the effect of annealing on structural, optical and photosensitive properties of deposited films. The photosensitivity of the CdSe film increased [64] upon annealing up to a temperature of 350 °C.

Sol-gel Technique

The sol-gel process can be used for depositing films on larger substrates. In the sol-gel process, the liquid precursor is laid out onto the substrate, followed by drying, and then firing. The operational cost of the sol-gel process is low because the process is very simple and does not need expensive equipment. Samarasekara and co-workers [65] studied structural properties multilayered cupric oxide thin films prepared by spin coating. Amin and co-workers deposited magnesium doped gallium nitride thin films by sol-gel and studied effects of the Mg concentration on the structural, surface morphology, elemental compositions, lattice vibrational and electrical properties of deposited films [66]. They found that by increases Mg concentration, the resistivity of the thin films decreases while the hole concentration and hall mobility of thin films increases. Nebi and co-workers deposited Co-doped TiO_2 films using sol-gel technique and estimated bandgap of deposited films [67].

Nanoparticle-Based Technique

Inks including dispersions of fine particles present assured advantages over pure solution-based methods, including a broader selection of liquid vehicles, the possibility to use more compact precursors with close-to-targeted composition and minimal presence of foreign, chemically bound species that have to be eliminated by thermal processing and that have the potential to reduce the critical thickness of the layers (i.e. the maximum thickness per layer that can produce a crack-free film). An early printing approach to deposit CZTS used particle-based (approx. 200 nm) precursors synthesized by reacting metal salts with sulfur in hot ethylene glycol [68]. Recently, a method was reported in which component binary and ternary metal chalcogenide nanoparticles were used rather than the multinary CZTS/Se particles to facilitate tailoring film composition, with efficiencies[69] as high as 8.5 %. Prasad and co-workers demonstrated NH_3 sensing properties of surface modified Ce-doped nanostructured ZnO thin films prepared by spray pyrolysis method [70].

Pingarron and co-workers demonstrated electrochemical biosensor based on gold nanoparticles [71]. Hassan and co-workers demonstrated a nanoparticle-based method for culture-free bacterial DNA enrichment from whole blood [72]. Hua and co-workers deposited multiple types of nanoparticle thin films by lithographic technique [73]. Sebastian and co-workers deposited green silver-nanoparticle-based dual sensor where they examined the optical and electrochemical sensing behavior of silver nanoparticles from Agaricus bisporus (AgNP-AB) for toxic Hg(II) ions [74]. Simonsen and co-workers demonstrated potential applications of magnetic nanoparticles in the petroleum industry, and they observed that the adsorption capacities for nanoparticles are around 90 % in case of water separation from emulsions [75]. Esfe and co-workers studied convective heat transfer and pressure drop of aqua based TiO_2 nanofluids of different diameters of nanoparticles by data analysis and modeling with artificial neural network [76]. Ashok and co-workers deposited SnO_2 nanoparticle for dye-sensitized solar cells applications and studied the electron transport characteristics of SnO_2 nanoparticles [77]. Georgiou and co-workers made copper nanoparticle metal grids for cost-effective ITO-free solution processed solar cells [78] and efficiency of 4.92 %. Nikam and co-workers deposited CdSe nanoparticles on ZnO nanorods photoanode for solar cell application using successive ionic layer adsorption and reaction (SILAR) technique at room temperature [79]. Vijayakumar and co-workers deposited vanadium carbide nanoparticles-based counter electrode for dye-sensitized solar cell [80].

Literature survey:

Thin film technology in protection against corrosion

Protection of metals and alloys from corrosion is of prime interest for different industrial processes and applications. The necessity of protection against corrosion has been driven from its costly damages. Corrosion is a “reaction” that takes place between metallic structures and its surrounding environment. Mechanistically, this reaction can be physical, chemical or electrochemical. The most significant is the electromechanical reaction, which involves the transfer of electrons between the reactants [81]. Several approaches and techniques have been adopted for protection against corrosion. Those included oxide film formations over metals and alloys [82], organic inhibitors [83]; different coatings approaches including inorganic [84], polymeric [85], spray [86], chemical vapor deposition [87], and anodization [88]. Chromate and phosphate phases provide excellent corrosion resistant coatings. However, they are restricted by environmental regulations in recent years [89] and are replaced with silicate, molybdate, rare earth, and titanium oxides or zirconium oxides [90]. Some techniques adopted for applying thin films for

corrosion protection and their pertinent applications are summarized in Table 1.

Recently, carefully designed coatings based on thin-film technologies have been introduced [91]. Coatings application to the surface of metals and alloys forms a physical or chemical barrier toward the corroding environment. This is achieved by hindering the migration of ionic species through the coating layer, or when the coating act as a sacrificial anode, or embedding an inhibitor to the coating film [92].

Specialty corrosion protecting coatings have been developed for advanced application such as aerospace industries [93]. In this respect, chemical and physical techniques have also been introduced such as sol-gel technique [94, 95]. Composite materials have several properties that encouraged their use as coating materials which improve corrosion protection efficiency. Among these properties: good adhesion characteristics, strain tolerance, self-healing characteristics, and heat conductivity [96]. Environmental, economic, technical and societal factors encouraged the use of hybrid materials [97]. The cost of the coating is another important issue for consideration, therefore readily available materials have been considered for film protection against corrosion [98, 99].

Table 1. Some techniques used for thin films application and their applications in corrosion protection.

Techniques	Applications
• **Spraying**	Gas turbine components
• **Thermal spraying**	Electrolytic cathode for copper refinement
• **Chemical vapour deposition,** • **physical vapour deposition**	• Water-cooled stator bars • Chips used in electrical generators
• **Screen printing** • **dip coating** • **thermal spraying**	• Semiconductor device and the liquid crystal device
• **Thermal spraying** • **Sputtering** • **Immersion** • **Chemical vapour deposition,** • **physical vapour deposition**	• Semiconductor processing equipment[98]
• **Spraying immersion roll coating**	• Alkaline-containing environment
• **Thermal spraying spray and fuse welding**	• High-temperature erosion-corrosion environments [99]

Graphene has attracted extensive attention for its unique properties including mechanical, chemical, electrical among others, and has found several advanced technical applications [100]. Some of the recent applications of graphene are sensors [101], energy storage and conversion [102] and electronics [103]. Graphene offers spectacular properties being inert, lightweight, atomically thin, impermeable, wear resistant and mechanical strength that promotes its application as a coating for corrosion protection [104]. The inert role of graphene in a corrosive environment showed new insight to develop anticorrosive coating layers on a metal substrate [24]. Due to its flexible and transparent nature, graphene as a coating can tolerate the curvature or roughness of the surface [105].

The basal plane of graphene offers chemical inertness and impermeability even to protons [106]. Acetone-derived graphene coating offered corrosion protection efficiency for copper in a seawater environment up to 37.5 times higher as compared to that of mechanically polished copper [107]. Further, investigation on the role of graphene coating on Cu surfaces suggests that the outstanding corrosion inhibition efficiency (IE) of 97.4 % is obtained by protecting the underlying copper (Cu) against the penetration of both dissolved oxygen and chlorine ions. The increase of graphene coating thickness increased inhibition efficiency up to 99 %, which can be attributed to the effective blocking of the ionic diffusion process. Graphene was grown by chemical vapor deposition over SUS304 stainless steel and on a catalyzing Ni/SUS304 double-layered structure [108]. A 3.5 wt% saline polarization test demonstrated that the corrosion currents in graphene-covered SUS304 were improved fivefold relative to the corrosion currents in non-graphene-covered SUS304. After a corrosion test, the graphene-covered stainless steel exhibited not only an excellent low interfacial contact resistance (ICR) of 36 mΩ cm^2 but also outstanding drainage characteristics. Other reports described the application of graphene as anti-corrosion and anti-oxidation coating on different substrates with different coatings [109-112].

Another approach was introduced by the formation of composite/hybrid structures of graphene and other materials for film formation over metal

substrates for protection against corrosion. Yang's group studied the fabrication of graphene reinforced waterborne polyurethane (PU) composite coatings on steel surfaces [113].

Functionalization of these graphene composites with titanate was employed to facilitate the dispersion of graphene in the composite coatings. When the graphene content was 0.2 wt %, three-dimensional random distribution of graphene was observed in the composite coatings, which gave an indirect path of electrolyte to penetrate through the coatings. When the graphene content reached 0.4 wt %, the graphene layers were self-aligned parallel to the substrate surfaces. Graphene reinforced polyphenylene sulfide (PPS) was reported that exhibited seven times higher wear life than pure PPS coating [114]. Graphene oxide was synthesized by the Hummer's method and then functionalized to yield graphene. The as-produced solution was coated on steel substrates through spray coating. The major wear form was identified as abrasive wear for graphene reinforced PPS coating whilst the wear form of pure PPS coating was adhesive wear.

Graphene/pernigraniline composites (GPC) were prepared by the *in situ* polymerization-reduction/dedoping method. The synthesized composites have a flake-like structure, and their conductivity is as low as 2.3×10^{-7} Scm^{-1}. The composites possess not only impenetrable property inherited from reduced graphene oxide but also insulating property inherited from pernigraniline. Potentiodynamic polarization and electrochemical impedance spectroscopy measurements revealed that the GPC-modified coating is outstanding barriers against corrosive media compared with pernigraniline or reduced GO modified films. Scratch tests also show that the corrosion-promotion effect of reduced GO in GPCs is inhibited. Similar studies reported preparation of nano-clay reinforced polyaniline composites and their coatings on steel surfaces [115]. The free-standing composite film exhibited a 400 % reduction in O_2 permeability compared to conventional polyaniline, which in turn offered significantly enhanced corrosion protection in the form of composite coatings. Recently, other several studies reported the use of graphene composites as anti-corrosion coatings [116-119].

Nanomaterials can be used to protect materials from tribocorrosion caused by simultaneous mechanical and chemical/electrochemical interactions between surfaces in relative motion. Nanomaterials such as FeCu/WC-Co and WC-Co, electrodeposited Ni-Co alloy, Ni-nano SiC, electroless Ni-p-nano SiC coatings and nanostructured titanium provide a lubricating effect that improves anti-trobocorrosion [120]. Ni-WC electrodeposition was achieved over stainless steel electrodes from an organic-free Watt's nickel chloride in the presence of suspended ultrafine WC particles [121]. The Watts' plating solution was composed of $NiSO_4$, $NiCl_2$, H_3BO_3 and WC powder (<1 μm). The solution pH was adjusted to 4.2, the temperature maintained at 50 ºC, and under stirring conditions, the applied current was 0.5 A cm^{-2} for 10 minutes. Ni-Co-WC was also electrodeposited from a bath containing the same composition as for Ni-WC composition. The microstructure developed between Ni-WC and Ni-Co-WC is a key factor in the development of dense and homogeneous surface resulting in hardness improvement. The hardness of the coating layer increased with the thickness. The Ni- WC coating with 8 g/L $NiCl_2$ in the electrodeposition bath realized the lowest corrosion rate for coated stainless steel in 0.1 M H_2SO_4. In another study, nickel hydroxide-graphene oxide composite coating was electrodeposited over 316-stainless steel by pulse current method [122].

A protection efficiency of 98.7 % against corrosion was achieved in sodium hydroxide containing solutions. The micro tribology measurements showed a decrease in the coefficient of friction for the nickel hydroxide-graphene layer that was strongly adsorbed to the stainless steel substrate. It was reported that the introduction of this layer coating provided an increase in the friction on the sample surface because of the rough surface provided by the aggregation of $Ni(OH)_2$ particles. Al_2O_3-SiC reinforced Ni-matrix nano-composite coatings were deposited on steel and nickel substrates using a constant current of 1 Adm^{-2} at 45 ºC in Watts bath of pH 4 for 60 minutes under stirring conditions [123]. The micro-hardness increased of the coatings increased in the order Ni-Al_2O_3<Ni-SC<Ni-Al_2O_3-SC while the wear rate showed the opposite trend with the lowest value reported for Ni-Al_2O_3-SC. The corrosion resistance behavior of these coatings was studied in 0.5 M Na_2SO_4 with the lowest corrosion current density obtained, and optimum passivation behavior was achieved when using the Ni-Al_2O_3-SC coating. The nucleation, growth mechanism and kinetics of electrodeposited Ni-Co-SiC composite-coating on carbon steel was studied by electrochemical techniques and atomic force microscopy [124]. Cyclic voltammetry and open circuit potential measurements indicated that Ni-Co-SiC requires more energy for its electrodeposition compared to Ni-Co coating. Atomic force microscopy data showed that more nucleation centers are formed for Ni-Co coating compared to Ni-Co-SiC formed after 2 seconds at -1.3 V (vs. SCE). The results showed that more nucleation is reached as the time of deposition increased and a uniform coating is formed after 60 seconds deposition time. It was also shown that the addition of SiC in the electrodeposition bath decreased the efficiency of nucleation. The authors indicated the formation of a clouding of inert particles around metal cations that increased the energy of transport of these cations to the cathode surface [124]. It was also reported that the electrochemical driving energy controlled by the applied negative potential on the cathode overruled the role played by SiC particles at high cathodic

current densities. A new generation of thin coatings are being developed and possess the property of self-healing based on inclusions that respond to different stimuli such as pH, humidity or mechanical stresses.

Meso-porous oxides core is introduced as the basis for the preparation of nano-containers [127].

The approach is based on a layer-by-layer assembly of oppositely charged species that prevented the self-release of the corrosion inhibitor to the electrolyte. The burst of the nano-container shell was induced by changing the pH value surrounding it, which in turn is in response to the nature of corrosion medium exposed to the coating [128]. Nanotechnology-based self-healing coatings have also been successfully introduced for corrosion protection of metals and alloys [129]. Self-healing approaches include corrosion conversion coatings, silane, sol-gel coatings with nano-reservoirs and conducting polymers.

Thin films materials can also be deposited on metallic surfaces using several techniques for different applications. Some of the commonly used methods are chemical vapor deposition (CVD), plasma enhanced CVD (PECVD), physical vapor deposition (PVD), pulse laser deposition (PLD), sputtering techniques and sol-gel methods.

Chemical vapor deposition for corrosion control has been discussed in a recent review [130]. The most commonly used PVD techniques are vacuum (by evaporation), sputter and arc vapour depositions. The coating resulting by PVD methods is hard but not completely uniform due to defects developed such as pores formation and columnar growth. The formed channels underneath the PVD coating allowed exposure of the underlying metal to the attacking electrolyte to diffuse in. For example, the Ti_2N film deposited over NdFeB resulted in the formation of pinholes and craters [131]. It is possible to control the quality of the resulting deposited film using PVD technique by adjusting the operational parameters. For example, the effect of the bias voltage of the substrate on the protection ability of chromium carbide film over AISI D2 steel was studied [132]. The authors found that the protection ability increased when the bias voltage decreased as indicated by the lowering in corrosion potential. It was also reported that the bias voltage used over the substrate decreased the corrosion resistance of the metal by developing a porous film of TiCN and TiNbCN on AISI 4140 [133]. In general, PVD coatings are vulnerable to aggressive attacks in chloride containing electrolytes. Surface defects developed from PVD deposition of thin films can be remediated by multilayers coatings. In this respect, a multilayer coating of Ti/TiN was investigated; the study showed enhancement in corrosion resistance for the coated steel in different electrolytes [134]. In another study, a double coating of Al_2O_2/Al/Ti over steel compared to $AlTiO_2$Ti or Al/Ti provided better corrosion resistance for steel in NaCl solution [135]. While double coating strategies could be effective in reducing the formation of surface defects In this respect, nano-structured carriers are loaded to the matrix of the coatings with different configurations to inhibit corrosion [125, 126].

using PVD technique, the method is relatively costly and time-consuming.

Pulsed laser deposition (PLD) can also be used for the deposition of thin-films over metallic substrates for corrosion protection. The method relies on the usage of short and highly energetic pulses to evaporate specific target particles that subsequently condense over the desired substrate. Some studies reported the use of PLD for depositing films such as corrosion protection of stainless steel using PLD of thin films of Y_2O_3 [136]. The study showed good protection of the Yttria layer to the steel substrate when exposed to molten uranium and actinide wastes. In another study, the parametric conditions of the PLD process were studied for the deposition of alumina over stainless steel substrate [137]. The results showed that average mass removal rate on laser fluency, ablation geometry and average deposition efficiency during PLD affected the structural and mechanical properties of alumina thin film formation over the steel substrate. The resulting α-alumina showed high corrosion resistance towards exposure to molten uranium up to a temperature of 1165 °C. The PLD technique faces some challenges such as the granular formation of thin film deposits that results in surface defects for corrosion protection application. For example, iron thin films deposited by PLD on silicon wafer resulted in the corrosion of the film when exposed to NaCl solution [138]. In this study, optical microscopy measurements showed localized corrosion at the peripherals of the particles within the iron film matrix. Therefore, PLD technique can be useful in the application for thin film deposition for corrosion protection in targeted purposes but still faces the challenge of high cost and the development of surface defects of some cases.

A chemical synthesis process based on sol-gel was also used successfully to deposit thin films over metallic substrates for corrosion protection [139]. The ultimate product formed by the sol-gel method is the formation of an oxide network through a chain condensation reaction of an inorganic metallic precursor [140]. Generally, a metal or metalloid alkoxide in the form of $M(OR)_n$ is an organic solvent is used as a precursor where M is Si, Ti, Al, Zr, Fe, etc. Sol-gel thin films were formed over a variety of surfaces for corrosion protection such as steels, stainless steel, aluminum, aluminum alloys, copper, magnesium, magnesium alloys, etc. The formed layer resulted in the formation of either of the following: metal oxide, organic/inorganic hybrid sol/gel, inhibitor-doped sol/gel and inorganic-metal sacrificing coatings. Si-, Zr-, Al-based oxides and alike possess high chemical stability that allowed good protection for the corresponding substrates in acidic media and under high-temperature operations [141]. Organic/inorganic hybrid sol-gel coatings suffered from some drawbacks

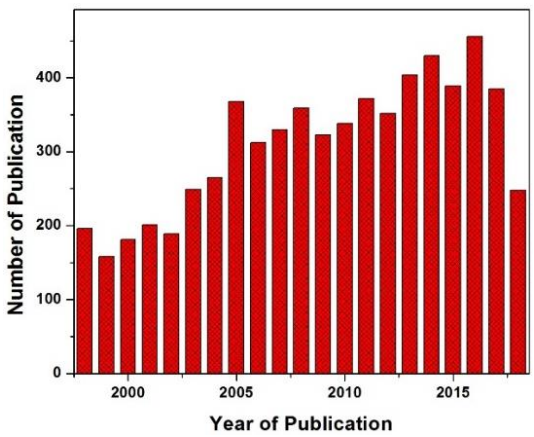
including cracks developed from rather thicker layers and the necessity of applying relatively higher temperature to cure the formed films [142]. Sol-gel layer could also be impregnated with an inhibitor to synergistically overcome corrosive medium for the metallic substrate. The strategy, in this case, depends on the incorporation of an organic inhibitor [143] or inorganic-based inhibitor. The addition of cerium acetate into the sol-gel layer reduced the amount of unreacted water-soluble silane and formed a passive ceria based film that resisted the chloride attack to the metal substrate.

An alternative approach using sol-gel method is to coat the substrate with inorganic metal-rich (sacrificed) coatings. The sacrificed metals such as zinc or magnesium were included in the sol-gel layer. This resulted in cathodic protection of the underlying metal substrate. Three coatings strategies have been adopted including post-cured, self-cured and self-cured approaches based on water-based alkali metallic silicates and solvent-based alkyl silicates, respectively [144]. A hybrid sol-gel impregnated with Mg primers was developed [145]. In this study, the coatings were sacrificed as a protecting element for aluminum alloys in 0.1% NaCl. However, in dilute Harrison solution, the rate of corrosion of the magnesium embedded in the sol-gel layer was relatively higher compared to the NaCl solution.

Thin film based gas sensors

Thin film based gas sensors are promising transducers used to detect a variety of oxidizing and reducing gases. This type of sensors is made up of various sensing elements in thin film form over a non-conducting substrates such as soda lime glass. The change in physical-chemical, optical and electrical properties of thin film materials in the presence of gas is the basic principle used to detect the various gases. The thin film gas sensors mainly consist of photo-resistive, thermo-resistive, piezo-resistive, magneto-resistive and chemo-resistive materials as a sensor element [146-150]. In the thermo-resistive sensors, the resistivity variation is controlled by the temperature, whereas piezo-resistive sensors use the change in resistance with mechanical stress. The photo-resistive sensors show sensing properties in the presence of UV/visible light, the magneto-resistive sensors based on the change in resistivity due to the presence of an external magnetic field. The chemo-resistive sensors measure the change in the resistivity produced by the interaction of a chemical substance with the sensing material [150]. However, among various gas sensors, a chemo-resistive thin film based gas sensors are promising because of the low cost and relative ease of operation, short response time, long life time, simple control electronics and highly sensitive to all ranges of the gases. However, relatively low sensitivity and poor specific selectivity, sensitive to the environmental factor and high operating temperatures are some of the drawbacks of the chemo-resistive gas sensors [151]. The materials utilized in these sensors are as often as possible prepared in thin film form, and they can be synthesized by various physical and chemical methods.

In the chemoresistive type of gas sensors, the metal oxides are the most suitable materials. The gas sensing process by a metal oxide involves two key functions such as identification of a target gas through a gas–solid interaction. The gas-solid interaction induces an electronic change of the oxide surface and followed by the transduction of the surface phenomenon into an electrical resistance change of the sensor [152]. However, the complex nature of the semiconducting oxide surface, including, porous, polycrystalline sensing bodies comprising nano-sized grains, the understanding of gas-solid interaction is not straightforward. Historically, Seiyama and co-workers [153] was the inventors of gas detection by metal oxide thin films. Soon after the work of Seiyama, Tagushi fabricated the first commercial gas sensor. Since then a large number of gas sensors were developed and fabricated using various materials including metal oxides, chalcogenides, polymers, graphite [154]. The commonly used metal oxides to fabricate gas sensors including, SnO_2, ZnO, In_2O_3, WO_3, Fe_2O_3, Ga_2O_3, Cr_2O_3, TiO_2, V_2O_5, HfO_2, $CdIn_2O_4$, $SrTiO_3$, and Li_2SnO_3 [155-160]. Fig. 6 and Table 2 show the number of publications on 'Thin Film Gas Sensors' from 1998 through mid-2018 (Source: Scopus Data). Fig. 6 and Table 2 show that the gradual increase in the publications was observed during the stated period.



Year of publication	Number of publication
1998	205
1999	188
2000	193
2001	205
2002	195
2003	257
2004	266
2005	383
2006	314
2007	315
2008	368
2009	320
2010	336
2011	382
2012	393
2013	411
2014	438
2015	380
2016	463
2017	392
2018	378

Figure. 6. Number of publications based on 'Thin Film Gas Sensor' from 1998 to mid of 2018 (Source: Scopus data).

Table 2. Number of publications based on "Thin Film Gas Sensor" from 1998 to 2018. (Source: Scopus data).

The important aspects of thin film gas sensors are a substrate, sensing elements, contacts, temperature and controller, chamber design, etc. As stated above, the most important sensing element are metal oxide semiconductors. There are two types of metal oxide semiconductors such as transition and non-transition type. The transition type metal oxide semiconductor contains more oxidation states as compared to its closest counterpart. The oxidation states are influencing factor on the requirement of the energy [161]. Therefore, transition-metal oxides are most often utilized as sensing elements, compared to the non-transition metal oxides. Also, transition-metal oxides with d^0 (such as WO_3, TiO_2, V_2O_5) and d^{10} (such as ZnO, SnO_2) electronic configurations are commonly reported as sensing element [162].

Additionally, the n-type metal oxide semiconductors are preferable in sensing research as compare to p-type semiconductors, even though they require a relatively lower operating temperature. Several other influencing factors, such as the nature of the surface, the structure of the sensing layer, defects, size affect the sensing properties of metal oxides as a gas sensing element. The gas sensing phenomenon is mainly a surface dependent activity; therefore, a higher surface area leads to the higher sensitivity of the thin film gas sensors. Therefore, nanosized thin film structure is a more suitable candidate than the bulk films. Also, the presence of the defects plays an important role in the gas sensing phenomenon. In particular, the oxygen-related defects or vacancies induce a large number of electron donor on the surface of metal oxides [163]. As a result of defects, a large number of electrons may capture from the conduction band of metal oxides to form a thicker electron depletion layer, which suggests the better response of the sensor. In addition to the defect concentration, the operating temperature plays an important role in the gas sensing properties of metal oxide thin film sensors. The metal oxide thin film sensors reported a higher sensitivity at the high working temperature. The possible reason is the higher reaction O^- species at an elevated temperature. In the fabrication of a thin film gas sensor, the sensor element layer has to be preheated to the desired temperature using micro-hotplate or filaments. At the higher working temperature, the probability of gas molecule adsorption is increased on the metal oxide layer surface. The ohmic contact is another factor influencing the gas performance of thin film gas sensors. The ohmic contact is a metal-semiconductor contact having negligible resistance. Particularly, the electric contacts with the sensing material should be ohmic. In general, the contacts should not interact with gas, and there should not be diffusion into the sensing material.

The progress of thin film gas sensors is acceptable for technological reasons. It is possible to prepare gas sensing devices with low power consumption and small size which can easily be integrated into an array.

Metal oxide semiconductors are the most studied sensing elements in thin film based gas sensors and showed the most satisfactory characteristics for gas detection. However, an extensive research effort should require to improve the knowledge of working mechanisms of thin film gas sensor and their long-term stability.

Thin film gas sensors were prepared via various physical and chemical synthetic routes. Also, a combination of physical and chemical method, another method is known as hybrid techniques, such as plasma deposition and reactive evaporation also have been reported to deposit a thin film gas sensor in the literature. Generally, in any synthesis method, three basic steps took place such as the creation of ions, transportation through suitable medium and condensation on the substrate. Among various physical thin film deposition method, thermal evaporation is relatively simple and convenient technique. In this technique, the target material vaporizes after heating to a suitable temperature. Then the vapour condensate onto a cooler substrate which forms thin solid films. However, the evaporated films are not uniform. The non-uniform film thickness occurs because the amount of the target material reaching the substrate depends on the angle between the source and the substrate surface [164]. It is well known that better quality thin films can be deposited by sputtering technique. Therefore, the number of publications on the deposition of thin film for gas sensor using sputtering are higher than evaporation technique. However, non-porous film formation by sputtering method restricts its wide applications for sensing purposes. Along with evaporation and sputtering techniques, a high vacuum method such as epitaxial deposition, laser deposition methods also used to prepare thin film based gas sensors [165]. The deposition of mono-layer by mono-layer is carried by epitaxial methods, but, the nanostructured and porous layer formation is difficult to achieve [166].

Meanwhile, chemical vapour deposition (CVD) is also a promising, versatile and flexible physical technique to deposit good quality thin films. The CVD method offers a simple set-up, the requirement of low-vacuum, easy to dope the impurities, etc. Therefore, about 50 research articles were published on CVD deposited thin film gas sensors. However, the complex reaction kinetics, high substrate temperature, difficulty in masking the substrate are some of the drawbacks of CVD.

The ease in commercial mass production, possibility to deposit controlled stoichiometric compounds, relatively pure products are the advantages of the physical techniques [167, 168]. Though, the gas sensing performance governed by the diffusion of gas through the pores of the sensing layers which can be enhanced by engineering the surface properties such as porosity, shape, surface area to volume ratio [169]. The physical techniques are not suitable to produce porosity, higher surface-to-volume ratio, therefore, they were not widely used to fabricate thin film gas sensors. On the other hand, the chemical or solution based deposition methods such as chemical bath deposition (CBD), electrochemical, sol-gel, spin coating, spray pyrolysis, hydro-solvothermal methods are appropriate to produce porous and nanostructured thin films, which are well suitable for gas sensing applications. Also, chemical methods give numerous surface morphologies to enhance surface-to-volume ratio. Less sophisticated experimental setups, low-cost equipment, no need of vacuum and requirement of lower temperatures for the depositions are additional advantages of chemical methods over the physical methods [170].

Electro-chemical deposition technique is well known solution based method used to coat metal oxides over the substrate with various morphologies. It requires an external source of current and conducting substrate for the deposition. In literature, very meager work is found on the electro-deposited thin film gas sensors. Meanwhile, the chemical solution deposition techniques are extensively used to fabricate thin film gas sensors. The easy to engineer the surface morphology, shape, porosity, surface area to volume ratio, the formation of defects via chemical methods harmonically results into the better sensing properties. Spray Pyrolysis, CBD and Sol-gel techniques are the most popular among chemical solution-based deposition methods. In the spray pyrolysis technique, an oxide thin film will have formed when a metallic salt solution is sprayed onto a hot substrate. The doped and mixed thin films can be prepared very easily by using the spray pyrolysis method.

Meanwhile, the CBD technique is mainly used for chalcogenide films. Recently, CBD has been extended to the deposition of metal oxide thin films. The CBD method is comprehensively used to fabricate thin film based gas sensors to detect various toxicants. However, the formation of the undesirable precipitate in the bulk of the solution is the main drawback of the CBD method. In order to avoid such precipitation, a CBD is modified (which is also known as successive ionic layer adsorption and reaction, SILAR or modified CBD (MCBD)). Recently, few reports were found on the formation of gas sensor deposited via SILAR technique. It has been reported that the performance of thin film gas sensors is improved by using chemical methods. In general, the chemical methods are the most appropriate techniques to deposit nanostructured and porous films. Also, doping is easy, and defects can be easily found in the chemically deposited film. All the factors are responsible for better sensing performance.

In addition to the deposition techniques, the nanostructure plays a very important role in the performance of thin film based gas sensors. Nano-materials has already demonstrated a range of highly sensitive and selective gas sensor designed for very low-power operation. In addition, the

nanostructured gas sensors can detect multiple gases simultaneously. The research on multiple gas detection is undergoing. Meanwhile, Fig. 7 shows the representation of nanostructured thin film gas sensors used to detect various gases.

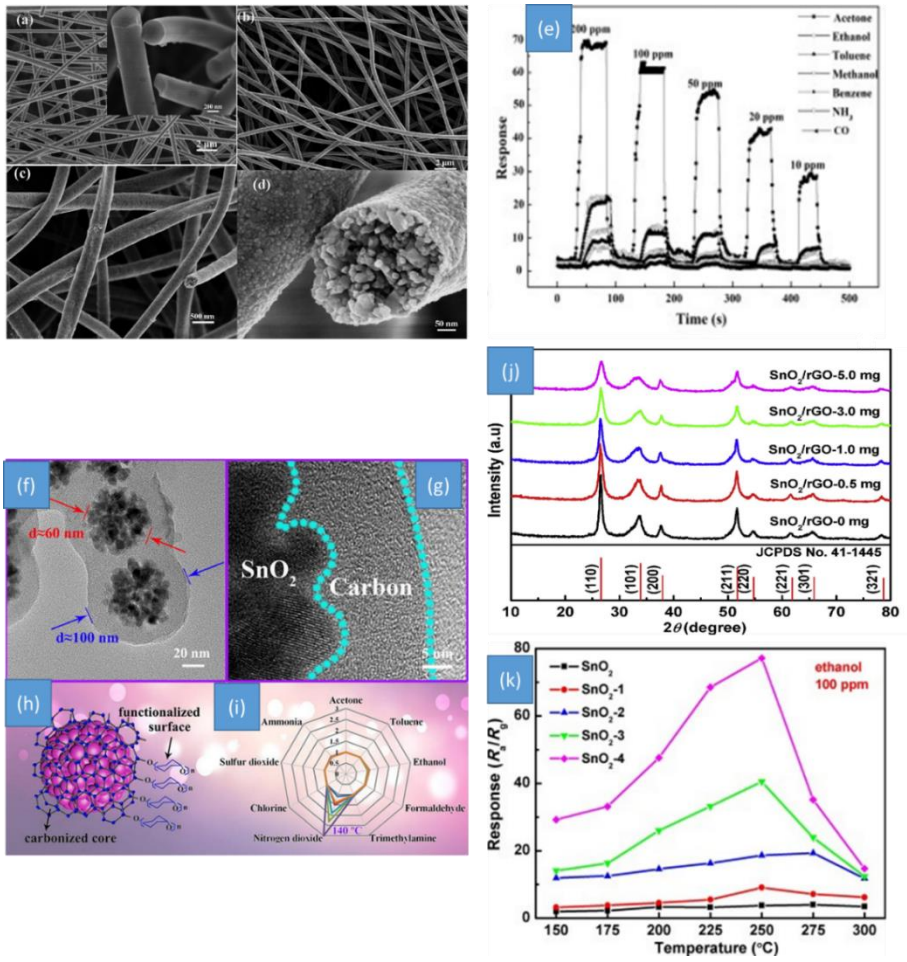


Figure 7. FESEM images of (a) PVP/AMT before calcinations (the inset shows the corresponding high magnification image); (b,c,d) WO_3 nanofibers after calcinations and (e) response and recovery characteristics of WO_3 based gas sensor to different gases [171], (f to i) a carbon materials-functionalized tin oxide nanoparticles-based sensing platform exhibits a highly selective response/recovery nitrogen dioxide behavior at a low working temperature of 140 °C with a low limit detection of 2 ppm [172], (f and g) enlarged TEM image of SnO_2/C core-shell nanospheres, (h and i) schematic of sensing mechanism diagram of SnO_2/C core-shell nanospheres-based sensor towards NO_2, and (j) XRD patterns of nanostructured SnO_2/rGO precursors and (k) Response versus operating temperature (150–300 °C) of the SnO_2 based sensors to 100 ppm ethanol (permission is taken from Elsevier) [173].

Conclusion:

There are several deposition methods (vacuum and non-vacuum deposition method) have been employed for depositing thin films. The obtained films were used for various applications such as gas sensor and corrosion protection as described by many researchers. Metal oxide semiconductors are the most studied sensing elements in thin film based gas sensors and showed the most satisfactory characteristics for gas detection.

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References:

1- Park J, Kim T, Denis S, Lee J, An S, Pyo Y, Lee D, Mo Y, Jin D, Chung H (2009) Flexible full color organic light emitting diode display on polyimide plastic substrate driven by amorphous indium gallium zinc oxide thin film transistors. Applied Physics Letters, https://doi.org/10.1063/1.3159832.
2- Jung WL, Jun D, Heo J, Jae SY (2013) Single material zinc sulfide bi-layer antireflection coatings for GaSa solar cells. Optics Express, 21, DOI:10.1364/OE.21.00A821.
3- Naoya T, So N, Hajime I, Yoshimi H, Saburo (2012) Magnetic shielding simulation of superconducting film magnetic shield covering

directly coupled HTS dc-SQUID magnetometer. Physics Procedia, 36, 138- 143.
4- Mark HK (1992) Magnetic thin films for data storage. Thin Solid Films, 216, 174-180.
5- Zhou J, Gao Y, Zhang Z, Luo H, Cao C, Chen Z, Dai L, Liu X (2013) VO thermochromic' smart window for energy savings and generation. Scientific Reports, DOI:10.1038/srep03029.
6- Ho SM, Anand TJS (2015) A review of chalcogenide thin films for solar cell applications. Indian Journal of Science and Technology, 8, DOI: 10.17485/ijst/2015/v8i12/67499.
7- Ho SM (2016) A brief review of the polymer thin film solar cells. International Journal of Scientific Research in Science, Engineering and Technology, 2, 1-5.
8- Ho SM (2016) Power conversion efficiency in thin film solar cell: a review. International Journal of Chemical Sciences, 14, 143-151.
9- Ali N, Hussain A, Ahmed R, Wang MK, Zhao C, Haq BU, Fu YQ (2016) Advances in nanostructured thin film materials for solar cell applications. Renewable and Sustainable Energy Reviews, 59, 726-737.
10- Lee TD, Ebong AU (2017) A review of thin film solar cell technologies and challenges, Renewable and Sustainable Energy Reviews, 70, 1286-1297.
11- Eliaz N, Shemesh G, Latanision RM (2002) Hot corrosion in gas turbine components. Engineering Failure Analysis, 9, 31-43.
12- Sivakumar R, Mordike BL (1989) High-temperature coatings for gas turbine blades: A review. Surface and Coatings Technology, 37, 139-160.
13- Sam Z, Deen S, Fu Y, Du H (2003) Recent advances of superhard nanocomposite coatings: a review. Surface and Coatings Technology, 167, 113-119.
14- Ruby D, Suman P (2011) Comparison of optical properties of bulk and nano crystalline thin films of CdS using different precursors. International Journal of Material Science, 1, 35-40.
15- William DN (1989) Mechanical properties of thin films. Metallurgical Transactions A, 20, https://doi.org/10.1007/BF02666659.
16- Zollner SZ, Demkov AA, Liu R, Fejes PL, Gregory RB, Alluri P (2000) Optical properties of bulk and thin film SrTiO3 on Si and Pt. Journal of Vaccum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement and Phenomena, 18, https://doi.org/10.1116/1.1303741.
17- K. Benyahia, A. Benhaya, M.S. Aida, ZnS thin films deposition by thermal evaporation for photovoltaic applications, Journal of Semiconductors, **2015**,
29- Y. Xu, W. Sun, X. Xiong, Z. Peng, Y. Chen, Z. Hao, Microstructure and properties of ZrC-SiC multi-phase coatings prepared by thermal evaporation deposition and an in-situ reaction https://doi.org/10.1088/16744926/36/10/103001
18- M. Nafiseh, M.R. Seyeed, C. Isabella, V. Alberto, Deposition of nanostructured CdS thin films by thermal evaporation method: effect of substrate temperature, Materials (Basel), **2017**, doi: 10.3390/ma10070773.
19- B.M.S. Sahuban, R. Chandramohan, T.A. Vijayan, K.S. Saravana, K.S.R. Sri, M. Jayachandran, A. Ayeshamariam, Effect of temperature of electron beam evaporated CdSe thin films, Journal of Material Sciences & Engineering, **2016**, DOI: 10.4172/2169-0022.1000297.
20- M.K. Jason, M.G. Russell, W.S. Sampath, Optimization of CdTe thin film solar cell efficiency usi8ng a sputtered, oxygenated CdS window layer, Progress in Photovoltaic, **2015**, https://doi.org/10.1002/pip.2578.
21- K. Anuar, S.M. Ho, S. Atan, H. Jelas, N. Saravanan, Chemical bath deposition of SnS thin films: AFM, EDAX and UV-Visible characterization, Oriental Journal of Chemistry, **2011**, 27, 1375-1381.
22- M.J. Haron, N. Saravanan, K. Anuar, S.M. Ho, W.T. Tan, S. Atan, Z. Kuang, Effect of deposition period and bath temperature on the properties of electrodeposited Cu_4SnS_4 films, Solid State Science and Technology, **2009**, 17, 226-237.
23- S.M. Ho, Influence of complexing agent on the growth of chemically deposited $Ni_3Pb_2S_2$ thin films, Oriental Journal of Chemistry, **2014**, 30, 1009-1012.
24- K. Anuar, S.M. Ho, K.S. Lim, N. Saravanan, SEM, EDAX and UV-Visible studies on the properties of Cu_2S thin films, Chalcogenide Letters, **2011**, 8, 405-410.
25- N. Memarian, S. Rozati, I. Concina, A. Vomiero, Deposition of Nanostructured CdS Thin Films by Thermal Evaporation Method: Effect of Substrate Temperature, Materials, **2017**, 10, 773-781.
26- T. Daniel, K. Mohanraj, G. Sivakumar, Effect of annealing temperature on thermally evaporated Cu_3SbS_3 thin films, Journal of Materials Science: Materials in Electronics, **2018**, 29, 9251-9257.
27- S. Jung, S. Ahn, J.H. Yun, J. Gwak, D. Kim, K. Yoon, Effects of Ga contents on properties of CIGS thin films and solar cells fabricated by co-evaporation technique, Current Applied Physics, **2010**, 10, 990-996.
28- V. Steinmann, R. Jaramillo, K. Hartman, R. Chakraborty, R. Brandt, J.R. Poindexter, Y.S. Lee, L. Sun, A. Polizzotti, H.H. Park, R.G. Gordon, T. Buonassisi, 3.88 % Efficient Tin Sulfide Solar Cells using Congruent Thermal Evaporation, Advanced Materials, **2014**, 26, 7488–7492.

method, Surface and Coatings Technology, **2018**, 349, 797-806.
30- E.D. McClanahan, N. Laegreid, **1991,** Production of thin films by controlled deposition of sputtered material. In: Behrisch R. Wittmaack K. (eds). Sputtering by Particle Bombardment III. Topics in Applied Physics, Springer, Berlin, Heidelberg, 64, 339-377.
31- O.P. Singh, R. Parmar, K.S. Gour, J.S. Tawale, S.P. Singh, V.N. Singh, Synthesis and characterization of petal type CZTS by stacked layer reactive sputtering, Superlattices and Microstructures, **2015**, 88, 281-286.
32- S. Siol, T.P. Dhakal, G.S. Gudavalli, P.P. Rajbhandari, C. DeHart, L.L. Baranowski, A. Zakutayev, Combinatorial Reactive Sputtering of In_2S_3 as an Alternative Contact Layer for Thin Film Solar Cells, ACS Applied Materials & Interfaces, **2016**, 8, 14004-14011.
33- K.S. Gour, A.K. Yadav, O.P. Singh, V.N. Singh, Na incorporated improved properties of Cu_2ZnSnS_4 (CZTS) thin film by DC sputtering, Vacuum, **2018**, 154, 148-153.
34- K.S. Gour, R. Parmar, O.P. Singh, V.N. Singh, Optimizing $CuInGaSe_2$ Thin Films Grown by Selenization of CuIn/CuGa Multilayers for Solar Cell Applications, Advanced Science, Engineering and Medicine, **2016**, 8, 314-318.
35- T.C. Gorjanc, D. Leong, C. Py, D. Roth, Room temperature deposition of ITO using R.F. magnetron sputtering, Thin Solid Films, **2002**, 413, 181-185.
36- J.H. Choi, A.A. Garay, S.M. Hwang, C.W. Chung, Influence of oxygen on characteristics of Zn(O, S) thin films deposited by RF magnetron sputtering, Journal of Vacuum Science & Technology A, **2015**, 33, 040603.
37- K.S. Gour, O.P. Singh, A.K. Yadav, R. Parmar, V.N. Singh, Effect of NaF evaporation on morphological and structural properties of $Cu_2ZnSnSe_4$ (CZTSe) thin film deposited by sputtering from a single compound target, Journal of Alloys and Compounds, **2017,** 718, 231-235.
38- K.S. Gour, O.P. Singh, B. Parmar, R. Husale, S. Senguttuvan, V.N. Singh, Enhanced photoresponse of $Cu_2ZnSn(S, Se)_4$ based photodetector in visible range, Journal of Alloys and Compounds, **2016**, 694, 119-123.
39- J.A. Obeng, G.L. Schrader, Reactive sputtering of molybdenum sulfide thin films, Surface and Coatings Technology, **1994**, 68, 422-426.
40- K.S. Gour, B. Bhattacharyya, O.P. Singh, A.K. Yadav, S. Husale, V.N. Singh, Nanostructured Cu_2ZnSnS_4 (CZTS) thin film for self-powered broadband photodetection, Journal of Alloys and Compounds, **2018**, 735, 285-290.
41- K.S. Gour, A. Yadav, R. Kumar, J.S. Tawale. V.V. Singh, Effect of Sulfurization Temperature on Optical and Compositional Properties of Sputtered Zn(O, S) Thin Films, Advanced Materials Letters, **2018**, 9, 811-815.
42- K.S. Gour, O.P. Singh, J.S. Tawale, V.V. Singh, Silver (Ag) incorporated Cu_2ZnSnS_4 thin film for improved optical and morphological properties, Superlattices and Microstructures, **2018**, 120, 54-59.
43- H.F. Huq, R.Y. Garza, R.G. Perez, Characteristics of GaN Thin Films Using Magnetron Sputtering System, Journal of Modern Physics, **2016**, 7, 2028-2037.
44- O.P. Singh, K.S. Gour, R. Parmar, V.V. Singh, Sodium induced grain growth, defect passivation and enhancement in the photovoltaic properties of Cu_2ZnSnS_4 thin film solar cell, Materials Chemistry and Physics, **2016**, 177, 293-298.
45- O.P. Singh, A. Sharma, K.S. Gour, S. Husale, V.N. Singh, Fast switching response of Na-doped CZTS photodetector from visible to NIR range, Solar Energy Materials & Solar Cells, **2016**, 157, 28-34.
46- J. Zhao, L. Hu, Z. Wang, Z. Wang, H. Zhang, Y. Zhao, X. Liang, Epitaxial growth of ZnO thin films on Si substrates by PLD technique, Journal of Crystal Growth, **2005**, 280, 455-461.
47- Y. Zeng, Y. Zhao, Y. Jiang, ZnO thin films prepared on titanium substrate by PLD technique at different substrate temperatures, Surface and Interface Analysis, **2014**, 46, 602-606.
48- M. Han, J. Jia, W. Wang, Pulsed laser deposition of a $Bi_2S_3/CuInS_2/TiO_2$ cascade structure for high photoelectrochemical performance, RSC Advances, **2016**, 6, 70952-70959.
49- T. Yamaki, T. Sumita, S. Yamamo, A. Miyashita, Preparation of epitaxial TiO_2 films by PLD for photocatalyst applications, Journal of Crystal Growth, **2002**, 237, 574-579.
50- M. Kotani, H. Miura, Y. Shim, K. Wakita, Composition-ratio control of CZTS films deposited by PLD, Physica Status Solidi C, 2**017**, 14, 1600212-1600216.
51- M.H. Rashid, J. Rabeya, M. Doha, O. Islam, P. Reith, G. Hopman, H. Hilgenkamp, Characterization of Single Step Electrodeposited Cu_2ZnSnS_4 Thin Films, Journal of Optics, **2018**, 47, 256-262.
52- S.M. Pawar, B. Pawar, A.V. Moholkar, D.S. Choi, J.H. Yun, J.H. Moon, S. Kolekar, J.H. Kim, Single Step Electrosynthesis of Cu_2ZnSnS_4 (CZTS) Thin Films for Solar Cell Application, Electrochimica Acta, **2010**, 55, 4057-4061.
53- F. Jiang, S. Li, C. Ozaki, T. Harada, S. Ikeda, Co-Electrodeposited Cu_2ZnSnS_4 Thin Film Solar Cell and Cu_2ZnSnS_4 Solar Cell – $BiVO_4$ Tandem Device for Unbiased Solar Water Splitting. RRL Solar RRL, **2018**, 2, https://doi.org/10.1002/solr.201700205.
54- B.P. Relekar, S.A. Mahadik, S. Jadhav, A.S. Patil, R.R. Koli, G.M. Lohar, V.J. Fulari, Effect of Electrodeposition Potential on Surface Free

Energy and Supercapacitance of MnO_2 Thin Films, Journal of Electronic Materials, **2018**, 47, 2731-2738.

55- K. Premnath, J. Theerthagiri, J. Madhavan, P. Arunachalam, M.A. Ghanem, M. A. Al-Mayouf, Electrodeposited $Co_{1-x}Mo_xS$ Thin Films as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction in Acid Medium, Journal of Solid State Electrochemistry, **2018**, 22, 2641-2647.

56- S. Thomas, J. Mallet, H. Rinnert, M. Molinari, Single Step Electrodeposition Process Using Ionic Liquid to Grow Highly Luminescent Silicon/Rare Earth (Er, Tb) Thin Films with Tunable Composition, RSC Advances, **2018**, 8, 3789-3797.

57- Y. Zhang, D.G. Ivey, Electrodeposition of Nanocrystalline CoFe Soft Magnetic Thin Films from Citrate- Stabilized Baths, Materials Chemistry and Physics, **2018**, 204, 171-178.

58- F.F. Xia, W.C. Jia, C.Y. Ma, R. Yang, Y. Wang, M. Potts, Synthesis and Characterization of Ni-Doped TiN Thin Films Deposited by Jet Electrodeposition, Applied Surface Science, **2018**, 434, 228-233.

59- B. Altiokka, A.K. Yildirim, Electrodeposition of CdS Thin Films at Various pH Values, Journal of the Korean Physical Society, **2018**, 72, 687-691.

60- L. Jiang, J. Chen, Y. Wang, K. Sun, F. Liu, Y. Lai, Graphene-Sb_2Se_3 Thin Films Photoelectrode Synthesized by in Situ Electrodeposition, Materials Letters, **2018**, 224, 109-112.

61- J.B. Thorat, S.V. Mohite, A.A. Bagade, T.J. Shinde, V.J. Fulari, K.Y. Rajpure, N.S. Shinde, Nanocrystalline Bi_2Te_3 thin films synthesized by electrodeposition method for photoelectrochemical application, Materials Science in Semiconductor Processing, **2018**, 79, 119-126.

62- W. Zhang, Y. Wu, J. Qi, M. Chen, R. Cao, A Thin NiFe Hydroxide Film Formed by Stepwise Electrodeposition Strategy with Significantly Improved Catalytic Water Oxidation Efficiency, Advanced Energy Materials, **2017**, 7, https://doi.org/10.1002/aenm.201602547

63- C. Devi, R.A. Kumar, E.R. Kumar, Effects of Heat Treatment on Structural, Optical and Magnetic Properties of Electro Deposited Fe–Ni–P Thin Films, Journal of Inorganic and Organometallic Polymers and Materials, 2018, 28, 1787-1792.

64- S. Mahato, A.K. Kar, The effect of annealing on structural, optical and photosensitive properties of electrodeposited cadmium selenide thin films, Journal of Science: Advanced Materials and Devices, **2017**, 2, 165-171.
Network, Physica E: Low-dimensional Systems and Nanostructures, **2018**, 97, 155-161.

65- P. Samarasekara, N. Premasiri, Structural Properties of Spin-Coated Multilayered Cupric Oxide Thin Films, Research & Reviews: Journal of Physics, **2015**, 4, 8-13.

66- N.M. Amin, S.S. Ng, Low-cost growth of magnesium doped gallium nitride thin films by sol-gel a spin coating method, IOP Conference Series: Materials Science and Engineering, **2018**, https://doi.org/10.1088/1757-899X/284/1/012031.

67- M. Nebi, D. Peker, S. Teme, Deposition of Co Doped TiO_2 Films Using Sol-Gel Spin Coating Technique and Investigation of Bandgap, AIP Conference Proceedings, **2018**, https://doi.org/10.1063/1.5026010.

68- T. Todorov, M. Kita, J. Carda, P. Escribano, Cu_2ZnSnS_4 Films Deposited by a Soft-Chemistry Method, Thin Solid Films, **2009**, 517, 2541–2544.

69- Q. Guo, Y. Cao, J. Caspar, W. Farneth, A.S. Ionkin, L.K. Johnson, M. Lu, I. Malajovich, D. Radu, K.R. Choudhury, H.D. Rosenfeld, W. Wu, A Simple Solution-Based Route to High-Efficiency CZTSSe Thin-Film Solar Cells, **2012**, 38th IEEE Photovoltaic Specialists Conference, Austin, TX, 2993-2996.

70- M.R. Prasad, M. Haris, M. Sridharan, NH_3 Sensing Properties of Surface Modified Ce-doped Nanostructured ZnO Thin Films Prepared by Spray Pyrolysis Method, Sensors and Actuators A: Physical, **2018,** 269, 435-443.

71- J.M. Pingarron, P. Yanez-Sedeno, A. Gonzalez-Cortes, Gold Nanoparticle-Based Electrochemical Biosensors, Electrochimica Acta, **2008**, 53, 5848-5866.

72- M.M. Hassan, A. Ranzoni, M. Cooper, A Nanoparticle-Based Method for Culture-Free Bacterial DNA Enrichment from Whole Blood, Biosensors and Bioelectronics, **2018**, 99, 150-155.

73- F. Hua, J. Shi, Y. Lvov, T. Cui, Patterning of Layer-by-Layer Self-Assembled Multiple Types of Nanoparticle Thin Films by Lithographic Technique, Nano Letters, **2002**, 2, 1219-1222.

74- M. Sebastian, A. Aravind, B. Mathew, Green Silver-Nanoparticle-Based Dual Sensor for Toxic Hg(II) Ions, Nanotechnology, **2018**, 29, https://doi.org/10.1088/1361-6528/aacb9a.

75- G. Simonsen, M. Strand, G. Oye, Potential Applications of Magnetic Nanoparticles within Separation in the Petroleum Industry, Journal of Petroleum Science and Engineering, **2018**, 165, 488-495.

76- M. Esfe, A.A. Nadooshan, A. Arshi, A. Alirezaie, Convective Heat Transfer and Pressure Drop of Aqua Based TiO_2 Nanofluids at Different Diameters of Nanoparticles: Data Analysis and Modeling with Artificial Neural

77- A. Ashok, S.N. Vijayaraghavan, G.E. Unni, S.V. Nair, M. Shanmugam, On the physics of

dispersive electron transport characteristics in SnO_2 nanoparticle-based dye sensitized solar
78- E. Georgiou, S.A. Choulis, F. Hermerschmidt, S. Pozov, I. Burgués-Ceballos, C. Christodoulou, G. Schider, S. Kreissl, R. Ward, Printed Copper Nanoparticle Metal Grids for Cost-Effective ITO-Free Solution Processed Solar Cells, RRL Solar, **2018**, 2, DOI: 10.1002/solr.201700192.
79- P.R. Nikam, P.K. Baviskar, S. Majumder, J.V. Sali, B.R. Sankapal, SILAR controlled CdSe nanoparticles sensitized ZnO nanorods photoanode for solar cell application: Electrolyte effect, Journal of Colloid and Interface Science, **2018**, 524, 148-155.
80- P. Vijayakumar, R. Govindaraj, N. Santhosh, M.S. Pandian, A. Pandikumar, P. Ramasamy, Investigation of Suitable Binder Combination and Electrochemical Charge Transfer Dynamics of Vanadium Carbide Nanoparticles-Based Counter Electrode in Pt-free Dye-Sensitized Solar Cell, Journal of Materials Science, **2018**, 53, 4444–4455.
81- M.G. Fontana, N.D. Greene, J. Klerer, Corrosion Engineering, McGraw Hill Education, 1968. doi:10.1149/1.2411256.
82- M. Froment, Passivity of metals and semiconductors- Proceedings of the fifth international symposium on passivity, 1983. https://www.elsevier.com/books/passivity-of-metals-and-semiconductors/froment/978-0-444-42252-1.
83- P.B. Raja, M. Ismail, S. Ghoreishiamiri, J. Mirza, M.C. Ismail, S. Kakooei, A.A. Rahim, Reviews on Corrosion Inhibitors: A Short View, Chem. Eng. Commun. 203 (2016) 1145–1156. doi:10.1080/00986445.2016.1172485.
84- P.S. Sidky, M.G. Hocking, Review of inorganic coatings and coating processes for reducing wear and corrosion, Br. Corros. J. 34 (1999) 171–183. doi:10.1179/000705999101500815.
85- M. Ates, A review on conducting polymer coatings for corrosion protection, J. Adhes. Sci. Technol., **2016**, 30, 1510–1536. doi:10.1080/01694243.2016.1150662.
86- S.M. Hassani-Gangaraj, A. Moridi, M. Guagliano, Critical review of corrosion protection by cold spray coatings, Surf. Eng., **2015**, 31, 803–815. doi:10.1179/1743294415Y.0000000018.
87- S. Sathiyanarayanan, G. Rajagopal, N. Palaniswamy, M. Raghavan, Corrosion protection by chemical vapor deposition: A review, Corros. Rev. 23 (2005) 355–370. doi:10.1515/CORRREV.2005.23.4-5-6.355.
88- Y. Wu, W. Zhao, W. Wang, L. Wang, Q. Xue, Novel anodic oxide film with self-sealing layer showing excellent corrosion resistance, Sci. Rep. 7 (2017) 1344. doi:10.1038/s41598-017-01549-y.
89- A.S. Hamdy, D.P. Butt, Environmentally compliant silica conversion coatings prepared by sol-gel method for aluminum alloys, Surf. Coatings Technol. 201 (2006) 401–407. doi: 10.1016/j.surfcoat.2005.11.142.
90- S. Shen, S. Cai, G. Xu, H. Zhao, S. Niu, R. Zhang, Influence of heat treatment on bond strength and corrosion resistance of sol-gel derived bioglass-ceramic coatings on magnesium alloy, J. Mech. Behav. Biomed. Mater. 45 (2015) 166–174. doi: 10.1016/j.jmbbm.2015.02.005.
91- M.F. Montemor, Functional and smart coatings for corrosion protection: A review of recent advances, Surf. Coatings Technol. 258 (2014) 17–37. doi: 10.1016/j.surfcoat.2014.06.031.
92- A.S.H. Makhlouf, I. Tiginyanu, New book Nanocoatings and Ultra-Thin Films: Technologies and Applications, First edit, Woodhead Publishing, 2011. https://www.sciencedirect.com/science/book/9781845698126.
93- D. Snihirova, S. V. Lamaka, M.F. Montemor, Smart composite coatings for corrosion protection of aluminium alloys in aerospace applications, in Smart Compos. Coatings Membr. Transp. Struct. Environ. Energy Appl., Elsevier, 2015: pp. 85–121. doi:10.1016/B978-1-78242-283-9.00004-X.
94- J. Gasiorek, A. Szczurek, B. Babiarczuk, J. Kaleta, W. Jones, J. Krzak, Functionalizable sol-gel silica coatings for corrosion mitigation, Materials (Basel). 11 (2018) 197. doi:10.3390/ma11020197.
95- R.B. Figueira, C.J.R. Silva, E. V. Pereira, Organic-inorganic hybrid sol-gel coatings for metal corrosion protection: a review of recent progress, J. Coatings Technol. Res. 12 (2015) 1–35. doi:10.1007/s11998-014- 9595-6.
96- M. Samadzadeh, S.H. Boura, M. Peikari, S.M. Kasiriha, A. Ashrafi, A review on self-healing coatings based on micro/nanocapsules, Prog. Org. Coatings. 68 (2010) 159–164. doi: 10.1016/j.porgcoat.2010.01.006.
97- R.G. Buchheit, S.B. Mamidipally, P. Schmutz, H. Guan, Active corrosion protection in Ce-modified hydrotalcite conversion coatings, Corrosion. 58 (2002) 3–14. doi:10.5006/1.3277303.
98- J. Ali Syed, H. Lu, S. Tang, X. Meng, Enhanced corrosion protective PANI-PAA/PEI multilayer composite coatings for 316SS by a spin coating technique, Appl. Surf. Sci. 325 (2015) 160–169. doi: 10.1016/j.apsusc.2014.11.021.
99- B.N. Grgur, A.R. Elkais, M.M. Gvozdenović, S. Drmanić, T.L. Trišović, B.Z. Jugović, Corrosion of mild steel with composite polyaniline coatings using different formulatons, Prog. Org. Coatings. 79 (2015) 17–24. doi: 10.1016/j.porgcoat.2014.10.013.
100- W. Choi, J. Lee, Graphene: synthesis and applications, First Edit, CRC Press, 2016.

101- A.G. Nada F. Atta, Hagar K. Hassan, Functionalized carbon-based materials for Nanosensors Chem. Biol. Appl., International Frequency Sensor Association Publishing S. L., Barcelona, 2017: pp. 262–319.
102- A. Galal, H.K. Hassan, T. Jacob, N.F. Atta, Enhancing the specific capacitance of SrRuO3and reduced graphene oxide in NaNO3, H3PO4and KOH electrolytes, Electrochim. Acta. 260 (2018) 738–747. doi: 10.1016/j.electacta.2017.12.026.
103- Y. Wu, D.B. Farmer, F. Xia, P. Avouris, Graphene electronics: Materials, devices, and circuits, Proc. IEEE. 101 (2013) 1620–1637. doi:10.1109/JPROC.2013.2260311.
104- L. Kyhl, S.F. Nielsen, A.G. Čabo, A. Cassidy, J.A. Miwa, L. Hornekær, Graphene as an anti-Corrosion coating layer, Faraday Discuss. 180 (2015) 495–509. doi:10.1039/c4fd00259h.
105- C. Sire, F. Ardiaca, S. Lepilliet, J.W.T. Seo, M.C. Hersam, G. Dambrine, H. Happy, V. Derycke, Flexible gigahertz transistors derived from solution-based single-layer graphene, Nano Lett. 12 (2012) 1184–1188. doi:10.1021/nl203316r.
106- R.R. Nair, H.A. Wu, P.N. Jayaram, I. V. Grigorieva, A.K. Geim, Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes, Science. 335 (2012) 442–444. doi:10.1126/science.1211694.
107- J.H. Huh, S.H. Kim, J.H. Chu, S.Y. Kim, J.H. Kim, S.Y. Kwon, Enhancement of seawater corrosion resistance in copper using acetone-derived graphene coating, Nanoscale, **2014**, 6, 4379–4386. doi:10.1039/c3nr05997a.
108- N.W. Pu, G.N. Shi, Y.M. Liu, X. Sun, J.K. Chang, C.L. Sun, M. Der Ger, C.Y. Chen, P.C. Wang, Y.Y. Peng, C.H. Wu, S. Lawes, Graphene is grown on stainless steel as a high-performance and ecofriendly anti-corrosion coating for polymer electrolyte membrane fuel cell bipolar plates, J. Power Sources. 282 (2015) 248–256. doi: 10.1016/j.jpowsour.2015.02.055.
109- M. Merisalu, T. Kahro, J. Kozlova, A. Niilisk, A. Nikolajev, M. Marandi, A. Floren, H. Alles, V. Sammelselg, Graphene-polypyrrole thin hybrid corrosion resistant coatings for copper, Synth. Met., **2015**, 200, 16–23. doi: 10.1016/j.synthmet.2014.12.024.
110- P.K. Nayak, C.J. Hsu, S.C. Wang, J.C. Sung, J.L. Huang, Graphene coated Ni films: A protective coating, Thin Solid Films. 529 (2013) 312–316. doi: 10.1016/j.tsf.2012.03.067.
111- A.S. Kousalya, A. Kumar, R. Paul, D. Zemlyanov, T.S. Fisher, Graphene: An effective oxidation barrier coating for liquid and two-phase cooling systems, Corros. Sci. 69 (2013) 5–10. doi: 10.1016/j.corsci.2012.12.014.
112- L.F. Dumée, L. He, Z. Wang, P. Sheath, J. Xiong, C. Feng, M.Y. Tan, F. She, M. Duke, S. Gray, A. Pacheco, P. Hodgson, M. Majumder, L. Kong, Growth of nano-textured graphene coatings across highly porous stainless steel support towards corrosion resistant coatings, Carbon N. Y. 87 (2015) 395–408. doi: 10.1016/j.carbon.2015.02.042.
113- Y. Li, Z. Yang, H. Qiu, Y. Dai, Q. Zheng, J. Li, J. Yang, Self-aligned graphene as an anticorrosive barrier in waterborne polyurethane composite coatings, J. Mater. Chem. A. 2 (2014) 14139–14145. doi:10.1039/c4ta02262a.
114- B. Pan, J. Zhao, Y. Zhang, Y. Zhang, Wear performance and mechanisms of polyphenylene sulfide/ polytetrafluoroethylene wax composite coatings reinforced by graphene, J. Macromol. Sci. Part B Phys. 51 (2012) 1218–1227. doi:10.1080/00222348.2011.627821.
115- J.M. Yeh, S.J. Liou, C.Y. Lai, P.C. Wu, T.Y. Tsai, Enhancement of corrosion protection effect in polyaniline via the formation of polyaniline - Clay nanocomposite materials, Chem. Mater. 13 (2001) 1131–1136. doi:10.1021/cm000938r.
116- A. Janković, S. Eraković, M. Mitrić, I.Z. Matić, Z.D. Juranić, G.C.P. Tsui, C.Y. Tang, V. Mišković-Stanković, K.Y. Rhee, S.J. Park, Bioactive hydroxyapatite/graphene composite coating and its corrosion stability in a simulated body fluid, J. Alloys Compd., **2015**, 624, 148–157. doi: 10.1016/j.jallcom.2014.11.078.
117- Z. Yu, H. Di, Y. Ma, L. Lv, Y. Pan, C. Zhang, Y. He, Fabrication of graphene oxide-alumina hybrids to reinforce the anti-corrosion performance of composite epoxy coatings, Appl. Surf. Sci. 351 (2015) 986–996. doi: 10.1016/j.apsusc.2015.06.026.
118- A. Galal, K.M. Amin, N.F. Atta, H.A. Abd El-Rehim, the Protective ability of graphene prepared by γ-irradiation and impregnated with organic inhibitor applied on AISI 316 stainless steel, J. Alloys Compd. 695 (2017) 638–647. doi: 10.1016/j.jallcom.2016.11.081.
119- N.F. Atta, K.M. Amin, H.A. Abd El-Rehim, A. Galal, Graphene prepared by gamma irradiation for corrosion protection of stainless steel 316 in chloride containing electrolytes, RSC Adv. **2015**, 5, 71627–71636. doi:10.1039/c5ra11287g.
120- T.S.N. Sankara Narayanan, Nanocoatings to improve the tribocorrosion performance of materials, in Corros. Prot. Control Using Nanomater., Elsevier, **2012**, pp. 167–212. doi:10.1016/B978-1-84569-949-9.50008-3.
121- N. Elkhoshkhany, A. Hafnway, A. Khaled, Electrodeposition and corrosion behavior of nano-structured Ni- WC and Ni-Co-WC composite coating, J. Alloys Compd. 695 (2017) 1505–1514.

doi: 10.1016/j.jallcom.2016.10.290.
122- C. Qiu, D. Liu, K. Jin, L. Fang, T. Sha, composite coating, Diam. Relat. Mater. 76 (2017) 150–156. doi: 10.1016/j.diamond.2017.04.015.
123- S. Dehgahi, R. Amini, M. Alizadeh, Corrosion, passivation and wear behaviors of electrodeposited Ni–Al2O3–SiC nano-composite coatings, Surf. Coatings Technol. 304 (2016) 502–511. doi: 10.1016/j.surfcoat.2016.07.007.
124- Y. Yang, Y.F. Cheng, Mechanistic aspects of electrodeposition of Ni-Co-SiC composite nano-coating on carbon steel, Electrochim. Acta. 109 (2013) 638–644. doi: 10.1016/j.electacta.2013.07.106.
125- D.G. Shchukin, H. Möhwald, Self-repairing coatings containing active nanoreservoirs, Small. 3 (2007) 926–943. doi:10.1002/smll.200700064.
126- A.E. Hughes, I.S. Cole, T.H. Muster, R.J. Varley, Designing green, self-healing coatings for metal protection, NPG Asia Mater. 2 (2010) 143–151. doi:10.1038/asiamat.2010.136.
127- E. V. Skorb, D. Fix, D. V. Andreeva, H. Möhwald, D.G. Shchukin, Surface-modified mesoporous SiO2 containers for corrosion protection, Adv. Funct. Mater. 19 (2009) 2373–2379. doi:10.1002/adfm.200801804.
128- G.B. Sukhorukov, E. Donath, S. Moy, Microencapsulation using step-wise adsorption of polyelectrolytes, J. Microencapsul. 17 (2000) 177–185. doi:10.1080/026520400288418.
129- M.G.S. Ferreira, M.L. Zheludkevich, J. Tedim, K.A. Yasakau, Self-healing nanocoatings for corrosion control, in: Corros. Prot. Control Using Nanomater., Elsevier, **2012**, 213–263. doi:10.1016/B978-1-84569-949-9.50009-5.
130- A. Shah, S. Izman, S.N.F. Ismail, M.H. Ayu, R. Daud, M.R. Abdul-Kadir, Physical vapour deposition on corrosion resistance: A review, APRN- J. Eng. Appl. Sci., **2018**, **13**, 3515-3523. ISSN 1819-6608.
131- T. Mashiki, H. Hikosaka, H. Tanoue, H. Takikawa, Y. Hasegawa, M. Taki, M. Kumagai and M. Kamiya, TiAlN film preparation by Y-shape filtered-arc deposition system. Thin Solid Films. 516 (2008) 6650-6654. doi.org/10.1016/j.tsf.2007.11.097.
132- C.C. Lin, J.-W. Lee, K.-L. Chang, W.-J. Hsieh, C.-Y. Wang, Y.-S. Chang and H.C. Shih, The effect of the substrate bias voltage on the mechanical and corrosion properties of chromium carbide thin films by filtered cathodic vacuum arc deposition. Surf. Coat. Tech. 200 (2006) 2679-2685. 10.1016/j.surfcoat.2005.01.029.
133- J.C. Caicedo, C. Amaya, L. Yate, W. Aperador, G. Zambrano, M.E. Gómez, J. Alvarado-Rivera, J. Muñoz-Saldaña and P. Prieto, Effect of applied bias voltage on corrosion-resistance for $TiC_{1-x}N_x$ and $Ti_{1-x}Nb_xC_{1-y}N_y$ coatings, Corrosion resistance and micro-tribological properties of nickel hydroxide-graphene ox Appl. Surf. Sci. 256 (2010) 2876-2883. doi.org/10.1016/j.apsusc.2009.11.042.
134- L.A.S. Ries, D.S. Azambuja, I.J.R. Baumvol, Corrosion resistance of steel coated with Ti/TiN multilayers. Surf. Coat. Tech., 89 (1997) 114-120. doi.org/10.1016/S0257-8972(96)03092-7.
135- J. Creus, H. Idrissi, H. Mazille, F. Sanchette, P. Jacquot, Corrosion behaviour of Al/Ti coating elaborated by cathodic arc PVD process onto mild steel substrate, Thin Solid Films, 346 (1999) 150-154. doi.org/10.1016/S0040-6090(98)01742-8.
136- A.K. Singh, T.R.G. Kutty, S. Sinha, Pulsed laser deposition of corrosion protective Yttrium Oxide (Y_2O_3) coating, J. Nucl. Mater. 420 (2012) 374–381. doi: 10.1016/j.jnucmat.2011.10.028.
137- A.K. Singh, S. Kaity, K. Singh, J. Thomas, T.R.G. Kutty, S. Sinha, Pulsed laser deposition of alumina coating for corrosion protection against liquid uranium, Mater. Chem. Phys. 143 (2014) 1446-1451. doi.org/10.1016/j.matchemphys.2013.11.063.
138- M. Okoshi, T. Maniwa, M. Hanabusa, Corrosion-resistant iron thin films formed by pulsed laser deposition with cast iron targets, Appl. Surf. Sci. 127–129 (1998) 462–465. doi.org/10.1016/S0169-4332(97)00673-9.
139- D. Wang, G.P. Bierwagen, Sol-gel coatings on metals for corrosion protection, Prog. Org. Coat. 64 (2009) 327–338. doi: 10.1016/j.porgcoat.2008.08.010.
140- C.J. Brinker, G.W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Harcourt Brace Jovanovich (Academic Press, Inc.), Boston, 1990.
141- P. Galliano, J.J.D. Damborenea, M.J. Pascual, A. Duran, Sol-Gel Coatings on 316L Steel for Clinical Applications, J. Sol–Gel Sci. Technol. 13 (1998) 723-727. doi.org/10.1023/A:100865320.
142- J. Wen, G.L. Wilkes, Organic/Inorganic Hybrid Network Materials by the Sol-Gel Approach, Chem. Mater., **1996**, 8, 1667-1681. doi.org/10.1021/cm9601143. [R 142- 62]
143- T. Sugama, J. Coat. Technol. Res., Cerium acetate-modified aminopropylsilane triol: A precursor of corrosion-preventing coating for aluminum-finned condensers, 2 (2005) 649-659.
144- F.N. Jones, M.E. Nichols, S.P. Pappas, Organic Coating Science and Technology, Fourth Edition, Wiley (1998) 99–114. doi:10.1002/9781119337201.
145- D. Battocchi, G.P. Bierwagen, Comparison of testing solutions on the protection of Al-alloys using a Mg-rich primer, Corros. Sci. 48 (2006) 2226-2240. doi.org/10.1016/j.corsci.2005.05.059.
146- E. Espid, F. Taghipour, UV-LED photo-

activated chemical gas sensors: A review, Critical Reviews in Solid State and Materials Sciences, 42 (2017) 416-43.
147- K. P. Kamloth, Semiconductor junction gas sensors, Chemical Reviews, 2008,108,367–399.
148- A. Kooser, R. L. Gunter, W. D. Delinger, T. L. Porter, M. P. Eastman, Gas sensing using embedded piezoresistive microcantilever sensors, Sensors and Actuators B: Chemical, 99 (2004) 474-479.
149- L. Jogschies, D. Klaas, R. Kruppe, J. Rittinger, P. Taptimthong, A. Wienecke, L. Rissing, M. C. Wurz, Recent developments of magnetoresistive sensors for industrial applications, Sensors, 15 (2015) 28665-28689.
150- A. M. Azad, S. A. Akbar, S. G. Mhaisalkar, L. D. Birkefeld, K. S. Goto, Solid-state gas sensors: A review, J. Electrochem. Soc., **1992**, 139, 3670-3709.
151- X. Liu, S. Cheng, H. Liu, S. Hu, D. Zhang, H. Ning, A survey on gas sensing technology, Sensors, **2012**, 12, 9635–9665.
152- S. Semancik, R.E. Cavicchi, The use of surface and thin film science in the development of advanced gas sensors, Applied Surface Science 70/71 (1993) 337-346.
153- T. Seiyama, A. Kato, K. Fujiishi, M. Nagatani, A new detector for gaseous components using semiconductive thin films, Analytical Chemistry, 34 (1962) 1502.
154- C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Metal oxide gas sensors: sensitivity and influencing factors, Sensors, **2010**, 10, 2088–2106.
155- W. Zhang, B. Yang, J. Liu, X. Chen, X. Wang, C. Yang, Highly sensitive and low operating temperature SnO_2 gas sensor doped by Cu and Zn two elements, Sensors and Actuators B: Chemical, 243 (2017) 982-989.
156- S. A. Vanalakar, V. L. Patil, N. S. Harale, S. A. Vhanalakar, M. G. Gang, J. Y. Kim, P. S. Patil, J. H. Kim, Controlled growth of ZnO nanorod arrays via wet chemical route for NO_2 gas sensor applications, Sensors and Actuators B: Chemical, 221 (2015) 1195-1201.
157- G. Sberveglieri, Recent developments in semiconducting thin-film gas sensors, Sensors and Actuators B: Chemical, 23 (1995) 103-109.
158- A. Dey, Semiconductor-metal oxide gas sensors: A review, Materials Science and Engineering: **2018**, B, 229, 206-217.
159- S. S. Shendage, V. L. Patil, S. A. Vanalakar, S. P. Patil, N. S. Harale, J. L. Bhosale, J. H. Kim, P. S. Patil, Sensitive and selective NO2 gas sensor based on WO_3 nanoplates, Sensors and Actuators B: Chemical, **2017**, 240, 426-433.
160- S. P. Patil, V. L. Patil, S. S. Shendage, N. S. Harale, S. A. Vanalakar, J. H. Kim, P. S. Patil, Spray pyrolyzed indium oxide thick films as NO_2 gas sensor, Ceramics International, **2016**, 42, 16160-16168.
161- M. K. Sofian, M. E. Oussama, A. A. Imad, C. K. Marsha, Semiconducting metal oxide based sensors for selective gas pollutant detection, Sensors, **2009**, 9 8158–8196.
162- C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Metal oxide gas sensors: Sensitivity and influencing factors, Sensors, **2010**, 10, 2088–2106.
163- V. L. Patil, S. A. Vanalakar, P. S. Patil, J. H. Kim, Fabrication of nanostructured ZnO thin films based NO_2 gas sensor via SILAR technique, Sensors and Actuators B: Chemical, **2017**, 239 1185-1193.
164- L. Holland, Vacuum Deposition of Thin Films (1956) Chapman and Hall Publication, London.
165- J. E. Greene, Review Article: Tracing the recorded history of thin-film sputter deposition: From the 1800s to 2017, Journal of Vacuum Science & Technology **2017**, A 35, 05C204.
166- T. M. Onn, R. Küngas, P. Fornasiero, K. Huang, R. J. Gorte, Inorganics 6 (2018) 34.
167- S. A. Vanalakar, G. L. Agawane, S. W. Shin, M. P. Suryawanshi, K. V. Gurav, K. S. Jeon, P. S. Patil, C. W. Jeong, J. Y. Kim, J. H. Kim, A review on pulsed laser deposited CZTS thin films for solar cell applications, Journal of Alloys and Compounds 619 (2015) 109-121.
168- S. A. Vanalakar, P. S. Patil, J. H. Kim, Recent advances in synthesis of Cu_2FeSnS_4 materials for solar cell applications: A review, Solar Energy Materials and Solar Cells 182 (2018) 204-219.
169- G. Kiriakidis, K. Moschovis, I. Kortidis, V. Binas, Ultra-low gas sensing utilizing metal oxide thin films, Vacuum, **2012**, 86, 495-506.
170- S.A. Vanalakar, Chemical synthesis of CdS, ZnO and CdS sensitized ZnO thin films and their characterization for photoelectrochemical solar cells. PhD dissertation, submitted to Shivaji Univ., Kolhapur, India, 2010, Jun. [Online]. Available: http://hdl.handle.net/10603/4064〉.
171- S. Wei, G. Zhao, W. Du, Q. Tian, Synthesis and excellent acetone sensing properties of porous WO_3 nanofibers, Vacuum, **2016**, 124, 32-39.
172- R. Zhang, X. Liu, T. Zhou, L. Wang, T. Zhang, Carbon materials-functionalized tin dioxide nanoparticles toward robust, high-performance nitrogen dioxide gas sensor, Journal of Colloid and Interface Science, **2018**, 524, 76-83.
173- C. Zhao, H. Gong, W. Lan, R. Ramachandran, H. Xu, S. Liu, F. Wang, Facile synthesis of SnO2 hierarchical porous nanosheets from graphene oxide sacrificial scaffolds for high-performance gas sensors, Sensors and Actuators B: Chemical, **2018**, 258, 492-500.