

CATALYST ROLE IN CHEMICAL VAPOR DEPOSITION (CVD) PROCESS: A REVIEW

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Abstract. The article describes significant role of catalyst in the deposition of various materials on different substrates surface via Chemical vapor deposition (CVD) process. CVD is a complex process of depositing thin coatings on a substrate surface via chemical reactions of gaseous materials. It is a useful process to produce materials of high purity, density and strength. It has emerged as a novel manufacturing technique in industrial sectors such as semiconductor and ceramic industries. Catalyst Enhanced Chemical Vapor Deposition (CECVD) is an enhancement method, used for the synthesis of nanomaterials on thermally sensitive substrates in the presence of appropriate metal catalysts. Such catalysts not only ensure the deposition to be carried out at considerably low temperature but they also produce films of high purity. The article provides the published data about nanomaterials synthesis by CECVD process. Catalytic chemical vapor deposition (CCVD) is another efficient and low-cost method for the mass production of highly pure carbon nanotubes (CNTs). In this process, CNTs are produced by the catalytic decomposition of hydrocarbon vapors. Cobalt, Iron, Nickel and their alloys are the most widely used catalysts in CNTs production through CVD process. This idea has been explained in detail with appropriate examples from recent literature.

1. INTRODUCTION

Chemical Vapor Deposition (CVD) is a synthesis process in which the chemical components react in the vapor phase close to or on a hot substrate. Activation of the substrate is usually performed by heating, radiation or plasma. This process produces a solid deposit. The deposition consists of either homogenous gas phase reactions taking place in the gas phase or heterogeneous chemical reactions which take place on/in close proximity of a hot surface resulting in the formation of powders or coatings respectively. The technique is systematically elucidated in Fig. 1. Materials with different proper-

ties can be produced by changing the substrate temperature, composition of the reaction gas mixture, total pressure gas flow, and experimental conditions, etc. [1,2]. For structural component applications, deposition usually occurs at a temperature of about 1000 °C. Reactive processes differentiate CVD from physical vapor deposition (PVD) processes such as physical evaporation, sputtering and sublimation processes [3].

Volatilization of a solid or liquid feed produces the gaseous compound containing the deposit material. A carrier gas (usually Hydrogen or Nitrogen) is then used to transport gaseous materials to hot

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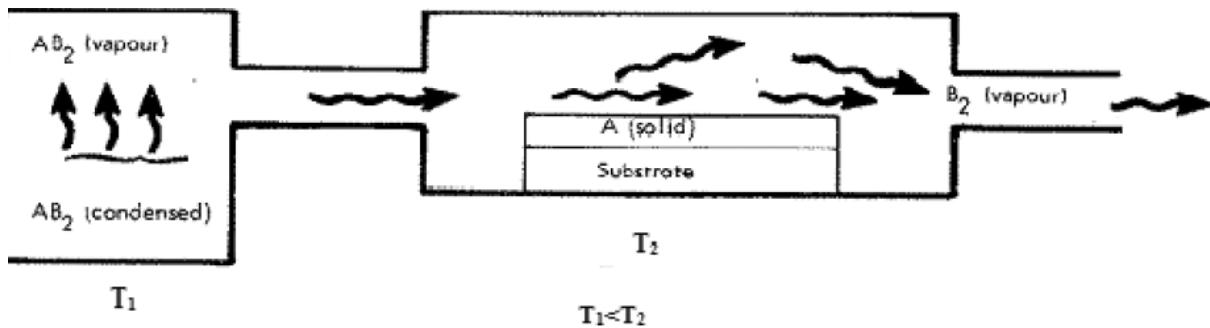
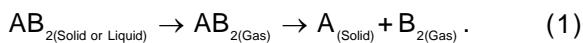


Fig. 1. Schematic illustration of a Chemical Vapor Deposition (CVD) process.

substrate. In a particular case of a transport, when the reactant and the deposit are of the same material, volatilization process is accompanied by reaction of the reactant with a gaseous transport agent. An opposite process would result in the formation of a solid deposit. Transport is dependent upon the variation in equilibrium constant for the temperatures of the substrate and reactant source [2,4]. It is imperative that all parts of the system are at least as hot as the vapor supply otherwise condensation of vapors will occur on their contact with any comparatively cool surface. The reaction part of the system is usually much hotter than the vapor supply. However, its temperature should be lower than the melting point of the deposit. It is also important to consider two other volatility aspects. (1) For the proper elimination of the unnecessary materials from the deposition system, they must be in gaseous form. (2) The deposit must have vapor pressure low enough to prevent its volatilization. The deposition reaction occurs either via thermal decomposition or via chemical reduction. A general example of such a reaction is represented by Eq. (1).



Mostly organometallic compounds are used in thermal decomposition. However, it is also applicable to halides and some other simple inorganic compounds. Sub-halides are being used at more modest reaction temperatures if the decomposition temperature of a halide is extremely high [5,6]. Similar types of reactants are employed in chemical reduction deposition. Buck made a survey of some reactant compounds appropriate for their application in the CVD process [7]. Hydrogen is frequently used as a reducing agent in chemical reduction. However, metal vapors can also be employed for this purpose. For example, reaction of zinc vapors with H_2S and water vapors results in the formation of ZnS and ZnO respectively [8,9]. The substrate can behave as a reductant as well. For example,

WF_6 is reduced by silicon [10]. Naturally, CVD is valuable for the production of a very thin deposit. One of the most important applications of chemical vapor deposition is the preparation of coatings and the manufacturing of materials to finished size for those substances which are not conveniently fabricated via more conventional ways. Such materials cannot be suitably fabricated either by physical vapor deposition or electrodeposition. High melting point elements such as carbon, tantalum or tungsten cannot be deposited by applying physical vapor deposition. While electrodeposition techniques cannot be used for some commercially significant elements such as silicon, molybdenum and tungsten [11]. CVD has an additional benefit as it is capable of depositing many alloys and some other compounds like carbides, oxides and nitrides. CVD materials have applications in various fields. Preparation of hard coatings of Al_2O_3 and TiC has been reported on cutting tools. Using deposits of materials such as tantalum, SiC , $MoSi_2$, and BN can offer protection against corrosion. Similarly coating of steel with tungsten can reduce corrosion. Fabricability of some materials is limited by conventional methods. Free standing shapes of such materials have been prepared by CVD. Most important among such materials are the refractory metals and their alloys. Most of the work is being focused on energy conversion and solid state electronic devices [12,13]. In a CVD process the deposition depends upon the thermal energy of the substrate. However, sometimes it is desirable to minimize the temperature of the substrate in order to protect the materials that have already been formed. For example, a film of aluminum formed via CVD process can be damaged by excessive heating. If a layer of aluminum already formed on a semiconductor wafer (substrate) is heated to a high temperature, it can diffuse into the substrate as well as the adjoining materials. The electrical performance of the aluminum will be badly affected resulting in the formation of a substandard semiconductor chip.

A number of methods have been developed to perform CVD at lower temperature, allowing the coatings to be grown at thermally sensitive substrates and therefore, improving the quality and purity of these coatings. These include the use of Plasmas, ion beams, reactive carrier gases, lasers and synchrotron etc. Plasma Enhanced Chemical Vapor Deposition (PECVD) is employed to accomplish high quality coating depositions at a reduced temperature. In this process, electron energy (plasma) is used as an excitation method in order to perform coating at a low temperature and at a moderate rate. In PECVD, the injected gases are activated by a radio frequency field. This results in the generation of a plasma zone containing free electrons, ionized gas molecules, free radicals and normal neutral gas molecules. Though in PECVD additional energy is provided which then causes thin films to be produced at a lower temperature. However, this process needs additional expense related to purchasing and plasma producing equipment. Furthermore, PECVD is carried out in vacuum, therefore, more sophisticated reactor need to be purchased. Similarly the use of high ion energy plasma (more than 20 ev) could cause serious damage to a few fragile substrates [14-16]. Due to the above drawbacks of the PECVD, use of catalysts is preferred to deposit thin films on thermally sensitive substrate. In certain CVD processes, catalytically active metals deposited act as autocatalysts. Seeding a surface with such active metals can lead to selective CVD on the seeded zones especially if a reactive carrier gas like oxygen or hydrogen is used too. It is believed that the adsorption and dissociation of the CVD precursor occur at the surface of the catalytically active metals since they act as reactive sites for these precursors. In the presence of a reactive carrier gas such as hydrogen or oxygen, a catalytically active metal serves for the elimination of the ligand fragments from the surface by catalytic oxidation or reduction respectively. Consequently, a clean surface is reproduced for additional precursor adsorption and decomposition. Therefore, it can be concluded that co-deposition of catalytically active material causes catalysis of the CVD of a noncatalytic material. Such a phenomenon can be termed as Catalyst-Enhanced Chemical Vapor Deposition (CECVD). In this process small quantity of a catalyst precursor is introduced in the reactor along with the major CVD precursor [17]. Catalytic Chemical Vapor Deposition (CCVD) or Hot Filament Chemical Vapor Deposition (HFCVD) is another simple and economic process which uses a hot filament for the chemical decomposition of the

precursor at the surface of already prepared catalyst particles supported on a surface. Since CCVD process is performed at low temperature (300–1200 °C) and ambient pressure, therefore, it is particularly useful for the synthesis of Carbon nanotubes (CNTs). The process can be performed using various carbon sources in any physical state. Furthermore, it allows the use of different substrates and ensures carbon nanotubes synthesis in a variety of forms like films and powder [18,19].

2. CATALYSTS USED IN CECVD PROCESS

Following metals have been found to be suitable as catalysts in CECVD process.

2.1. Palladium

Palladium is considered to be a highly active catalyst for both hydrogenation as well as oxidation. Further, it provides an active surface for CVD of other metals [20-23]. Zhang and his coworkers chose palladium as catalyst component for CECVD. They also used palladium complexes as precursor in the CECVD of Yttria (Y_2O_3) and Zirconia (ZrO_2). These precursors were found to be useful in lowering the temperature of yttria and zirconia coatings from their β -diketonate precursors. They observed that no carbon impurities were found and the palladium content was low enough to be detected by XPS analysis under optimum conditions. Coatings were grown on several substrates including aluminum, platinum, silicon, and glass and titanium nitride. All these substrates showed brilliant adhesion [17]. In another attempt, they used CECVD technique to grow high quality pure coatings of yttrium oxide from $[\text{Y}(\text{thd})_3]$ ($\text{thd} = 2,2,6,6\text{-tetramethyl-3,5-heptanedionato}$), using oxygen as a carrier gas. Several palladium compounds were employed as catalyst precursor. The Palladium complexes used as catalyst ensured the CVD of Yttria from $[\text{Y}(\text{thd})_3]$ to be carried out at much milder conditions than in their absence. Characterization of yttria coatings by XPS (X-ray Photoelectron Spectroscopy) SEM (Scanning Electron Microscopy) and XRD (X-ray Diffraction) techniques confirmed their open amorphous structures [24]. Jianhua *et al.* used $\text{Pd}(\text{hfac})_2$ and $\text{Pd}(3\text{-methylallyl})(\text{acac})$ as catalysts for the CVD of Palladium-Platinum bilayer nanofilms on polysulfone. They reported the deposition of thin films of palladium, platinum and their bilayers on polysulfone substrate. Use of Pd complexes as catalyst caused the CVD process to be performed at a significantly low temperature. The films were grown at the rate of

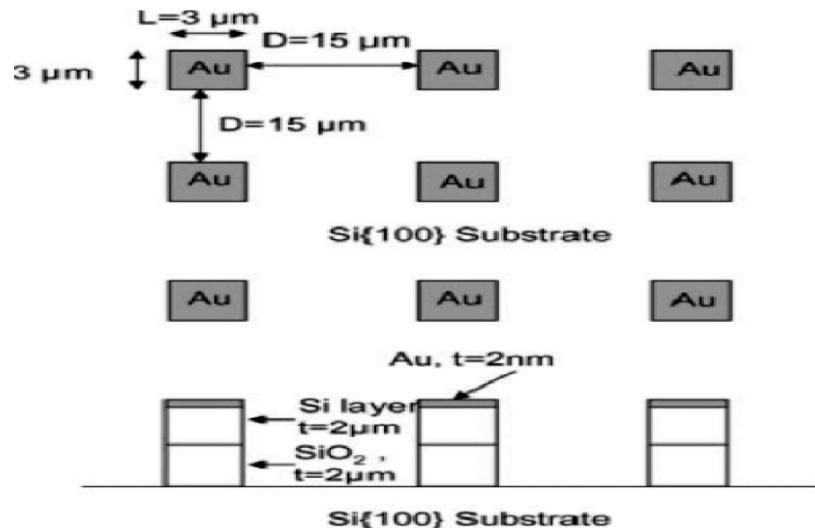


Fig. 2. Schematic representation of a gold-dot pattern on a silicon substrate, reprinted with permission from H. Suzuki, H. Araki, M. Tosa and T. Noda // *Materials Transactions* **48** (2007) 2202, © 2007 The Japan Institute of Metals and Materials.

350-450 nm/h. They used oxygen and Nitrogen as carrier gas at 220-300 °C at normal pressure. The particle size was reported to be about 15-30 nm while the thickness of the Pt-Pd bilayer was found to be 120-180 nm [25]. Deposition of Pd and Pt and their alloy on polyimide by CECVD has also been reported. $\text{Pd}(\text{hfac})_2$ and $\text{Pd}(3\text{-methylallyl})(\text{acac})$ were applied as catalysts. In CECVD of Pd, Pt and their alloy films on polyimide, $\text{Pd}(\text{hfac})_2$ and $\text{Pd}(3\text{-methylallyl})(\text{acac})$ were found particularly useful under oxidative or reductive conditions. During this process oxygen and nitrogen were used as carrier gases. For the alloy film formation, co-deposition of Pd and Pt complexes was performed under O_2 at 300 °C. The atomic ratios of Pd/Pt changed with changing deposition conditions. The alloy was found to be free from the contamination of carbon and fluorine. It contained 37.2% palladium and 62.8% platinum [26,27]. Endong *et al.* used CECVD for the deposition of nanosized nickel on Teflon. Different nickel complexes served as precursors. Palladium compounds $\text{Pd}(\text{hfac})_2$, PdCl_2 , and $\text{Pd}(\eta^3\text{-2-methylallyl})\text{acac}$ were used as catalyst. These catalysts significantly decreased the CVD temperature (180-250 °C). Hydrogen gas served as a carrier gas. Substrate and precursors temperature controlled the film growth rate. Characterization of Ni granular films by XPS and SEM showed that the films had shiny silvery color. The particle size was recorded to be 50-140 nm. XPS analysis also confirmed 90-95% purity of the Ni film [28]. Potochnik and his coworkers developed a method for selective chemical vapor deposition of adherent, conductive copper films on SiO_2 , Si, and diamond using a Pd-based cata-

lyst. Chemical vapor deposition of copper was carried out in a cold-walled reactor at 171-183 °C. The catalyst greatly enhanced the deposition of copper on the substrate surface [29].

2.2. Gold

Gold has been successfully applied as a catalyst in CECVD process. In recent times, silicon nanostructures have attracted significant attention due to their potential of being probable building blocks for nanoelectronics [30-32]. Wei and his coworkers used metal-catalyzed CVD method for the synthesis of single crystal silicon nanobelts. Gold was used as a catalyst which greatly improved the formation of nanomaterials. The length of silicon nanotubes was recorded to be more than 100 μm. These nanotubes were 0.2 to 2 μm wide. Furthermore these nanomaterials were reported to have flat surfaces, smooth edges and tiny thickness [33]. Synthesis of silicon nanowires (SiNWs) from thermal cracking of disilane by CVD, using Gold as a catalyst, has been reported. The SiNWs were grown on {100} silicon wafers coated with Gold and {100} silicon-on-insulator wafers at a temperature below 300 °C. Silicon nanowires were formed at temperature lower than 250 °C. Gold particles present on the substrate surface assisted in their growth. Disilane was decomposed to form a liquid Au-Si eutectic on gold particles at a low temperature. The phase diagram of Au-Si reveals that the solubility of Si in solid Au is extremely small. Thus at liquid-solid interface, pure silicon precipitated. As 363 °C is the eutectic temperature of Au-Si, SiNWs were

formed at a lower temperature than the melting points of Au and Si [34], see Fig. 2.

Crystalline GaN nanorods have been developed by Au-Assissted CVD in an atmosphere of NH₃ at an elevated temperature under ambient pressure. Si was used as a substrate. X-ray diffraction (XRD), Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used for the characterization of these nanorods. SEM images showed a nanoparticle cap on the end of each nanorod. Presence of such cap confined the diameter of nanorod [35]. Hofmann *et al.* used gold as catalyst for the selective growth of silicon nanowires at temperature below 400 °C via plasma enhanced chemical vapor deposition. Silane was used as silicon source. In this work gold proved to be a very useful catalyst because it did not form a silicide and the bulk Au/Si eutectic temperature was comparatively low (363 °C) as compared to other catalysts like Ti and Fe. The Si nanowires showed a clean crystalline silicon core enclosed by a 2 nm thick oxide sheath. Variation in the catalyst thickness did not have any effect on the diameter of the Silicon nanowires. However, use of a thicker Au layer resulted in the formation of amorphous worm like structures [36]. Han *et al* developed high-quality single crystal gallium nitride nanowires by applying gold nanoparticles as catalyst. Song claimed that this method has the potential to get control over several important aspects of the growth, i.e. control of the nanowires diameter by using monodispersed gold clusters, control of the nanowires location via e-beam patterning of the catalyst sites, and control of the nanowires orientation via epitaxial growth on α -plane sapphire substrates [37]. Gao and his co-workers obtained CdS nanobelts as single crystalline with wurtzite structure by simple thermal evaporation of CdS powders in the presence of Au catalyst. These nanobelts are of several hundred nanometers in width, tens of micrometers in length, and tens of nanometers in thickness. Au catalyst nanoparticles initiated the growth of CdS nanobelts via a catalyst-assisted vapor-liquid-solid process, and a side growth along the belt width direction via a vapor-solid process [38].

2.3. Nickel

Nickel is another metal which has been used successfully as a catalyst in catalyst enhanced chemical vapor deposition process for the growth of thin films of various materials. Huang and his coworkers used Ni(NO₂)₃ as a catalyst for the preparation of high quality α -Si₃N₄ nanobelts. They used better

chemical vapor deposition method (CVD) via direct reaction of Si vapor with flowing Nitrogen at 1450 °C on the carbon felt deposited with Ni(NO₂)₃. The α -Si₃N₄ nanobelts prepared by this method were 40-60 nm thick, 200-300 nm wide and up to few millimeters long.VLS (vapor-liquid-solid) base growth method caused their preliminary nucleation and proton nanobelt development in the catalyst droplets and later base growth [39]. Cimalla and his coworkers used Ni as a catalyst for the growth of AlN nanowires via metal organic chemical vapor deposition. These nanowires had a diameter of 20 nm and were grown stochastically via vapor Liquid solid process. Ni catalyst played a key role in the formation AlN nanowires by this method [40]. Wei *et al.* have successfully fabricated GaN nanowires on Si(111) substrates through chemical vapor deposition method by applying NiCl₂ as catalyst. The obtained results reveal that GaN nanowires are single-crystal with hexagonal wurtzite structure and possess high crystalline quality. These nanowires are several tons of microns in length with size of 20-50 nm in diameter. Some nano-droplets were also observed on their tips, which demonstrate that growth mechanism of GaN nanowires shows agreement with Vapor-liquid-Solid (VLS) process. NiCl₂ catalyst assists the fabrication of single-crystal GaN [41]. Further, Saxena *et al.* has proved the importance of nickel sulfate catalyst in the synthesis of carbon nano-fibers by using thermal chemical vapor deposition method. The nano-fibers were obtained by the decomposition of turpentine oil in the presence of nickel sulfate catalyst and had a diameter of approximately 3-5 μ m on the graphite surface [42]. The growth of high purity aluminum nitride nanowires has been successfully achieved via catalyst assisted chemical vapor deposition. For this purpose pure aluminum powder was coated on the substrate and ammonia was passed through the furnace at 1200 °C. Ni was used as a promising metal catalyst in the chemical reaction to grow these high quality nanowires. Ni catalyst played a vital role in the control of the nanostructure morphology. A route for the formation of high quality nanowires was provided by the nucleation of AlN with metal catalyst assisted reaction. Results gave a direct evidence of vapor-solid-liquid growth mechanism for the synthesis of this high quality, uniform nanowires. SEM images revealed that the nanowires were capped with the catalyst metal droplets at the tip [43]. Lourie *et al* has developed BN nano-tube of controlled diameters and wall thickness by using monodisperse nickel boride particles as catalyst. The BN nano-tubes resemble those grown by the higher temperature

arc-discharge and laser-ablation methods. Nickel boride catalyst replaced temperature and laser parameters to grow the same BN nano-tubes [44]. GaN nanowires have been prepared by Ni-assisted metal-organic chemical vapor deposition method. Electron diffraction, X-ray energy dispersive energy spectrometry and high-resolution transmission electron microscopy were used to reveal the structure and chemistry of the catalyst particles. The obtained results showed that the catalyst particles are Ni_3Ga with an ordered $L\text{I}_2$ structure. Further it was suggested that the catalyst was a solid particle during growth. Therefore under these conditions a vapor-solid-solid mechanism was suggested for the growth of GaN nanowires [45].

2.4. Iron

Iron has also been reported to be a useful catalyst in CECVD process. Chemical Vapor deposition of SiH_4 gas at 450 °C under the catalysis of Fe particles produced single-crystal silicon nanowires with the prism structures. Iron particles situated at the tip of the carbon nanotubes (CNTs) were used as a catalyst. Transmission electron microscopy (TEM) revealed that these silicon nanowires had a diameter of 50-70 nm. Their length was recorded to be several microns. Both CNTs and Fe catalyst played a significant role in the growth process of SiNWs [46]. Su *et al.* used Iron supported catalysts ($\text{Fe}/\text{SiO}_2\text{-Al}_2\text{O}_3$) for the large scale synthesis of Boron nitrides nanotubes (BNNTs) at a low temperature in a plasma assisted chemical vapor deposition system. Ammonia and diborane were used as precursors. The BNNTs prepared were crystalline with tubular structures. Further they were reported to possess preferential zigzag arrangement. Boron dissolved in iron precipitated and reacted with nitrogen. It formed BN sheet on catalyst surface [47]. Shang and his coworkers used Fe films as catalysts for the synthesis of large area open ended tubular graphite cones (TGCs) via microwave plasma assisted chemical vapor deposition method. Fe catalyst was found only at the base of the TGCs indicating that they were formed by base-growth mechanism. Fe played a crucial role to control the growth of TGCs. The density of TGCs was recorded to be $5.8 \times 10^5 / \text{cm}^2$ whereas the average growth rate was 0.6 $\mu\text{m}/\text{min}$. An apex angle of 2.5° was recorded for the sharpest TGC [48].

2.5. Miscellaneous

Zardo and his coworkers reported the growth of silicon nanowires by plasma enhanced chemical va-

por deposition using gallium as a catalyst. Oxidation of gallium was prevented by the used of plasma and thus its catalytic role was maintained. The growth direction of the nanowires was found to be dependent on temperature and gallium thickness. Gallium was found at the end of the nanowires. These results lead to good improvement towards discovery of new catalysts to gold for the synthesis of nanowires [49]. They also successfully applied Indium as a catalyst for the synthesis of silicon nanowires from silane via plasma enhanced chemical vapor deposition. The indium droplets were exposed to hydrogen plasma so as to promote its catalytic activity. Electron microscopy and Raman spectroscopy revealed that the structure of the nanowires is a function of the growth conditions. The nanowires crystallized along the <111>, <112> or <001> growth direction [50]. Yoon et al. prepared carbon nano-fibers with a fast growth rate of 0.9 $\mu\text{m}/\text{s}$ through thermal CVD process by using Co nano-particles as catalyst. Co nanoparticles provided template in the formation of nano-fibers. Size and shape of Co catalyst has a significant impact on the diffusion of carbon atoms and nucleation of carbon nanofibers. However, the growth rate of nanofibers was also controlled by the flow rate of acetylene and hydrogen [51].

3. CARBON NANOTUBES SYNTHESIS BY CATALYTIC CHEMICAL VAPOR DEPOSITION (CCVD) PROCESS

Carbon nanotubes (CNTs) are self-organized nanoscale allotropes of carbon. They possess superb mechanical, chemical and electrical characteristics. Therefore, they are likely to have numerous uses. A number of methods have been reported for the synthesis of carbon nanotubes e.g. laser ablation, arc discharge and catalytic chemical vapor deposition. Arc discharge method was first used to develop multi-walled carbon nanotubes (MWNTs). Single-walled carbon nanotubes (SWNTs) were grown by laser-ablation process. Among these methods, catalytic chemical vapor deposition has been found to be the most suitable technique as it needs much lower temperature than both laser ablation and arc discharge methods. In CCVD, metal catalyst nanoparticles (usually transition metals such as Fe, Co or Ni) are prepared on substrate surface which is put in the furnace. The nanoparticles are then subjected to reduction by heating them under hydrogen or ammonia. A hydrocarbon gas is passed into the furnace. Carbon monoxide can also

be used as a carbon source. Methane and acetylene are the two widely used gaseous carbon sources used for this purpose. Liquid carbon sources such as methanol and ethanol are heated and then an inert gas is used to transport their vapors into the furnace. Single-walled carbon nanotubes (SWCNs) have been synthesized at a comparatively low temperature (550 °C) by using alcohol as carbon sources. Catalytic decomposition of the hydrocarbon particles over metal catalyst nanoparticles results in carbon deposition at a temperature ranging from 500–1200 °C [52–54]. The diameter of the CNTs formed is usually dependent on the physical dimensions of the metal catalyst. The unusual ability of the transition metals to produce graphitic carbon is considered to be related to a number of factors which include their catalytic ability to decompose the volatile carbon source, the formation of metastable carbides and the diffusion of carbon through metal catalyst particles [55]. A well-established mechanism for CVD is based on the hypothesis of hydrogen release and carbon absorption into the metals surface after decomposition of the parent hydrocarbon. The overall energy gradient of the reaction is balanced by the exothermic decomposition of the hydrocarbon and endothermic crystallization of carbon species over the metal surface. Furthermore, the catalyst-metal interaction can be weak or strong leading to two different types known as “tip growth model” and “base growth model” respectively. In the former case, there is a longer CNT production while shorter is expected in the latter one. Single or multi-walled nature of CNTs is greatly controlled by the size of the catalytic particle i.e. smaller particles support single-walled CNTs formation and vice versa [56].

4. CATALYSTS USED IN CCVD PROCESS

Transition metals have been found suitable catalysts for CNT synthesis. For CCVD synthesis of CNTs, generally, nanometer-size metal particles have been found to be suitable as they facilitate precursor decomposition at a lower temperature than the spontaneous temperature required for the decomposition of the precursor. From literature study, it is evident that Fe, Ni, Co, and Mo have been widely used metal catalysts, mainly because of (a) high solubility of carbon in these metals at high temperatures and (b) high diffusion rate in these metals. Moreover, low equilibrium vapor-pressure and high melting points of these metals provide a wide range of temperature for a variety of precursors [57].

Majority of the articles available in the literature regarding the CNTs growth in the presence of iron based catalysts, describe the synthesis of MWNTs [58–74]. However, a few groups have also synthesized SWNTs [75–84]. Nickel-based catalysts have generally been used for the synthesis of MWNTs [69,85–87]. Occasionally, such catalysts have proved to be useful for the growth of SWNTs [88–90]. Most of the research work on Cobalt-based catalysts has also resulted in the growth of MWNTs [91–97]. However, a few groups have also obtained SWNTs with such catalysts [89,90,98]. Apart from Fe, Co, and Ni, noble metals such as Cu, Au, Ag, Pd, and Pt have also been reported to be useful catalysts for the CNTs synthesis via CVD process. Compared to transition metals, noble metals behave differently as they possess exceptionally low solubility for carbon. However, their small particle size (less than 5 nm) has been found to be useful for carbon solubility during CNTs growth [99,100]. Lee and his co-workers used tungsten-based catalysts for the synthesis of highly pure, well aligned, multi-walled CNTs through CVD process [101]. Moisala *et al.* have published a comprehensive review on the role of metal catalysts in synthesis of CNTs via CVD [102]. Alloy of different metals such as Iron-cobalt, [103,104] Iron-Molybdenum [105] and Cobalt-Molybdenum [106] considerably increase the yield of CNTs via CCVD. Apart from the above metals, semi-conductors such as Si, Ge, and oxide nanoparticles like SiO_2 , TiO_2 , Al_2O_3 , La_2O_3 , and Er_2O_3 have also been reported to catalyze the growth of SWNTs via CVD process. These findings challenge the traditional concept that metals are required for SWNTs growth via CVD process [107]. For carbon nanotubes synthesis via CVD, a number of catalyst preparation methods are available. One of them is to pattern the catalyst on the substrate. Sol-gel technique, ion exchange, incipient wetness impregnation and organometallic grafting are the other catalyst preparation routes which are adapted during carbon nanotubes synthesis [108].

5. EXPERIMENTAL EVALUATION OF VARIOUS CATALYSTS IN CCVD PROCESS

Maoshuai *et al.* used silica supported monometallic nickel catalyst for the synthesis of single-walled carbon nanotubes (SWNTs) via thermal chemical vapor deposition method. The catalyst supported the synthesis of small diameter SWNTs at comparatively low temperature (450 °C to 800 °C). Different spectroscopic techniques such as photolu-

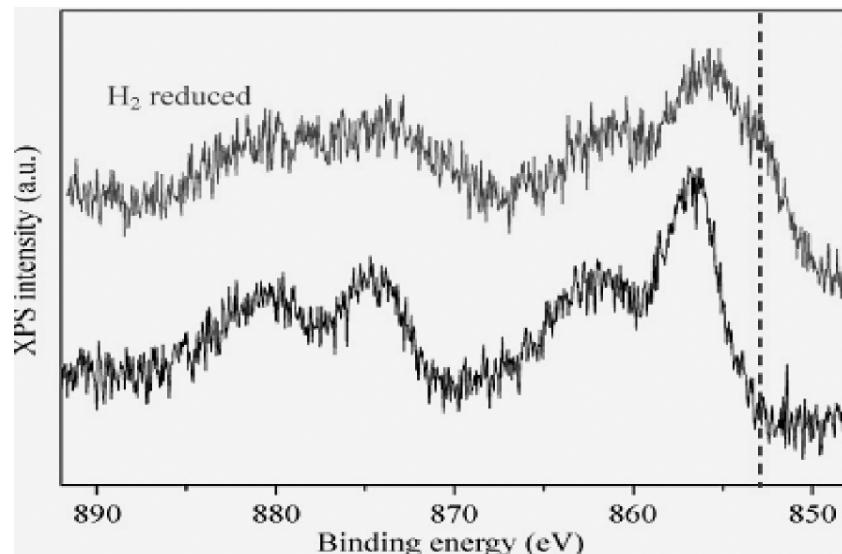


Fig. 3. Ni 2p XPS spectra of as prepared and reduced Ni/SiO₂ catalysts. The red dashed line denotes the peak position of metallic Ni, reprinted with permission from He Maoshuai, A. I. Chemov, E. D. Obraztsova, J. Sainio, E. Rikkinen, H. Jiang, Z. Zhu, A. Kaskela, A. G. Nasibulin, E. I. Kauppinen, M. Niemela and O. Krause // *Nano Res.* **4** (2011) 334, © 2011 Springer.

minescence emission (PLE), Raman spectroscopy and X-ray photoelectron spectroscopy were used to assess the single-walled carbon nanotubes (SWNTs) grown over Ni catalyst at various temperatures [109], see Fig. 3.

Coiled carbon nanotubes were synthesized by Ni-catalyzed pyrolysis of acetone dissolved acetylene (97%). A small quantity of co-catalyst PCl₃ was also introduced along with acetylene gas. However, the role of later component was not convincingly obvious. Ni catalyst was loaded on a graphite plate substrate. The substrate was heated to 500–800 °C in an electric furnace [110]. Chatterjee and his co-workers reported the synthesis of CNT by catalytic CVD from the pyrolysis of turpentine oil. Finely divided cobalt metal (obtained by the decomposition of cobalt nitrate) was used as a catalyst. SEM and TEM images of these CNTs showed that they are closely packed having a diameter of 10–50 nm. From the resistivity measurements, these CNTs were found to be of significantly conducting nature [111]. Iron as a catalyst and MgO as a substrate have been reported to be one of the most suitable catalyst-substrate combinations for the production of carbon nanotubes by catalytic chemical vapor deposition method. In such CNT synthesis, acetylene was used as carbon source on MgO powder substrate infused with iron nitrate solution. The temperature was kept 500–800 °C in this process [112]. Farzaneh *et al.* prepared carbon nanotubes by the catalytic chemical vapor deposition of ethane at 550 °C in a 2 h time. Nanoparticles of Ni-Ce-Zr were

employed as catalyst. Characterization of the nanotubes was performed by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The diameter of these carbon nanotubes was recorded to be 45 nm. Carbon nanotubes of helical (diameter of 50 nm) and curved (diameter of 90 nm) morphologies were obtained by using Ni-Ce mixed oxides or NiO₂ respectively [113]. Cobalt-nickel alloy catalyst was used for the production of a large quantity of straight CNTs by chemical vapor deposition. Acetylene was used as carbon source at 820 °C. The CNTs possessed better graphitization, straightness, great inner diameter and fewer defects than curved nanotubes. Due to these characteristics, this method is valuable for the prospective utilization of carbon nanotubes [114]. Ansaldi *et al.* reported the effect of various catalyst preparations in an ethanol-CVD process for SWCNT onto silicon substrate. This process had advantages like simplicity, low synthesis temperature, higher yield and producing high quality nanotubes. They also reported comprehensive comparison among various catalyst preparations at different temperatures [115]. Adams *et al.* studied the role of different chemical components of a catalyst system employed in producing CNTs by chemical vapor deposition (CVD). They found that molybdenum plays a vital role in CNT growth and Y-junction and solvent can affect the crystallinity of product. Their investigations revealed that growing multiple samples of CNTs of various compositions simultaneously resulted in interaction

from one sample to neighboring one [116]. Wang *et al.* reported a new method of depositing aligned single and double-walled CNTs by using a mixture of C_2H_2/NH_3 gas following microwave plasma-assisted CVD. They improved the efficiency of catalyst by using the elevated substrate temperatures and manipulation of the Fe catalyst thickness which resulted in growth of well graphitized vertically aligned CNTs. [117] Chen *et al.* used the alkali-reducing pretreated hydrogen storage alloy ($MINi_{4.0} Co_{0.6} Al_{0.4}$) powder as catalyst and prepared CNTs following the CVD and observed that the surface modification of the alloy is effective to provide the catalytic active sites for the growth of CNTs. These composites of CNTs have advantage of being used as hydrogen storage material [118]. Carbon nanotubes have been grown on Co-Ni catalytic metal particles deposited SiO_2 substrate via thermal chemical vapor deposition. The growth was achieved at a low temperature (500-550 °C) with the help of co-catalysts like Pd, Pt and Cr. It was observed that Pd was the most effective co-catalyst for the reduction of temperature in the carbon nanotubes growth. Pd co-catalyst produced noodle-like CNTs of 60-80 nm at 500 °C. Curled carbon nanofibres were grown by using Cr co-catalyst at 550 °C [119]. Valentini *et al.* obtained CNTs by plasma enhanced chemical vapor deposition in the presence of Ni catalyst. They reported that the nanotubes growth took place via the diffusion of carbon into the Ni catalyst particle, present on the nanotube tip. They further concluded that CNTs growth was dependent on Ni layer thickness because no growth was observed for a layer thickness above 20 nm [120]. Choi and his coworkers deposited thin Ni films (of 70 nm thickness) by using rf magnetron sputtering on Si substrates. They used Microwave Plasma Enhanced Chemical Vapor Deposition (MPECVD) for CNTs growth on Ni-deposited Si substrates at 700 °C, applying a gas mixture of CH_4 (20%) and H_2 (20%) as precursor. From their experiments, they concluded that diameter, growth rate and density of the vertically aligned CNTs were dependent on the microstructure of Ni thin films. Furthermore, variation in surface morphology of the Ni catalyst controls the CNTs growth [121]. Yudasaka and his coworkers investigated the specific conditions for the CNTs synthesis via CVD process catalyzed by Ni. They used Ni particles having a diameter of 10-500 nm for CNTs growth via CVD of 2-methyl-1,2-naphthyl ketone at 1000 to 600 °C. They observed the CNTs formation at 700 °C when Ni particles of 20-30 nm diameters were used as catalyst [85]. Metallic carbon is considered to be a contaminant in the CNTs growth. However, Zhou

et al. successfully synthesized SWNTs via Cu-catalyzed CVD process. They applied two types of copper nanoparticles as efficient catalysts on silicon wafers or silica spheres at an optimum temperature of 825-850 °C. Monodispersed copper nanoparticles (with the size of about 10 nm) were prepared by the reduction of $CuCl_2$ with cetyltrimethylammonium bromide (CTAB) solution. Similarly, they also used Cu_2O nanoparticles (prepared by the thermolysis of cupric formates in coordinating solvents) as catalyst. It was revealed that the weaker interactions between Cu and SiO_2 played a key role in the formation of random SWNT network as well as horizontally aligned SWNT arrays [122]. Recently, Li and his coworkers discovered some new catalysts for the synthesis of single-walled carbon nanotubes (SWNTs). Cu was observed as a very suitable catalyst for growing SWNT arrays on silicon as well as quartz substrates. Pb is a remarkably useful catalyst for growing SWNTs without any metallic contamination. SWNTs developed with these catalysts have been found to be appropriate for manufacturing high-performance nanodevices [123]. Zhu *et al.* have synthesized double-walled nanotubes (DWNTs) by catalytic chemical vapor deposition (CCVD). A mixture of CH_4 and H_2 was caused to flow over supported metal catalysts. These catalysts were obtained by the decomposition of $Fe(CH_3COO)_2$ and $Co(CH_3COO)_2$ on mesoporous silica. Transmission electron microscopy (TEM) revealed a large percentage of DWNTs in zones where tubular layered structures could be clearly resolved [124]. Bi *et al.* reported an unconventional CVD method for the synthesis of high-quality carbon microcoils (CMCs) and wave-like carbon nanofibers (WCNFs) using Ni-P alloy as catalyst. This simple and high-throughput technique can be used to control the morphology and structural properties of a wider range of carbon-based micro and nano-materials [125]. Lee *et al.* reported the influence of Fe, Co, and Ni on the CNTs synthesized via thermal CVD of C_2H_2 gas and CNTs grown on these three different catalyst particles under the same conditions revealed almost same morphology irrespective of the catalyst used. However, the crystallinity of CNTs was dependent on the catalyst. Therefore, growth rate, the diameter and the crystallinity of CNTs can be tuned by the selection of the catalyst [126]. Laser-treated high surface area vanadium pentoxide has been reported as a catalyst support for the synthesis of carbon nanotubes via catalytic chemical vapor deposition (CCVD). The synthesis was performed by the decomposition of acetylene at 720 °C using Fe, Co, and Ni as catalyst. Decomposition of acetylene in

the presence of iron catalyst supported on vanadia produced carbon nanotubes of well graphitized walls. While amorphous or fiber like material was obtained by the decomposition of acetylene over cobalt and nickel catalysts [127]. Synthesis of multi wall carbon nanotubes (MWNTs) has been investigated in the presence of iron, Cobalt and mixture of iron and Cobalt supported on Al_2O_3 and SiO_2 . Acetylene served as carbon source while nitrogen gas was used as a carrier gas. The decomposition of acetylene was carried out at 500, 600, and 700 °C. MWNTs of high yield and best quality were obtained in the presence of mixture of Iron and Cobalt catalyst supported on alumina prepared from aluminum isopropoxide [128]. Atthipalli *et al.* explored that a Ni enriched surface on the bulk copper foil substrates assisted the growth of dense vertically aligned carbon nano-tubes when using a thermal CVD method with additional Fe catalyst supplied during the growth. A single thin Ni layer is more beneficial in the growth of precise carbon nano-tubes as compared to others that use multiple barriers films of different thickness which would also add to the contact resistance. Furthermore, xylene/ferrocene mixture is critical for the growth of carbon nano-tubes by applying only nickel film [129]. Li *et al.* developed multi-walled carbon nano-tubes with the diameters from 15 to 50 nm and length from several microns to several tens of microns by using Ni/Al composite catalyst through CVD of methane at temperature range of 450 to 650 °C. Growth rate, diameter and crystallinity of CNTs can be controlled by varying the synthesis temperature and catalyst composition [130]. Multi-walled carbon nano tubes have been reported to be grown by thermal chemical vapor deposition in the presence of Ni and Fe as catalysts. Two types of multi-wall CNTs were grown depending on the type of catalyst. When iron was used as a catalyst, the synthesized CNTs had spiral structure and curled shape. While in the presence of Ni catalyst, CNTs of bamboo-like structure and straight shape were formed. Both types of CNTs have been reported to possess the tip-growth mechanism [131]. Pradhan and his coworkers synthesized SWNTs from methane at low temperature using Fe and Fe/Mo metallic and oxide catalysts in the CVD process. They observed that in the presence of these catalysts SWNTs were obtained at low temperature (680 °C) and low methane flow rate (40 cc/min). The reduced Fe catalyst was found to be active even at these mild conditions. Further, it was observed that at the same conditions, addition of 20 wt.% Mo (i.e. Fe: Mo = 5:1) was enough to activate the catalyst in oxide form i.e. activation in H_2 was not found

to be necessary even at 680 °C temperature. Addition of 20 wt.% Mo to the Fe-catalyst gave synergistic benefit. They did not observe the co-production of MWNTs [132]. Chatterjee *et al* used finely divided Co metal catalyst for the synthesis of highly dense and intrinsically n-type carbon nanotubes from the decomposition of turpentine oil at 675 °C through CVD process. These nanotubes were found suitable for electrochemical and electronic applications due to their low resistance [133]. A combination of Ruthenium Chloride, Iron(III) nitrate, nanohydrate, and alumina nanoparticle catalyst mixture placed on silicon chips under the ultra-low gas flow process via CVD produced long carbon nanotubes (over 800 microns in length). Many of the CNTs showed alignment parallel to the gas flow [134].

6. APPLICATIONS OF CECVD AND CCVD PROCESSES

Catalyst enhanced chemical vapor deposition (CECVD) is a useful process to produce thin films of high purity on thermally sensitive substrates at low temperature. Therefore, catalyst enhanced chemical vapor deposition (CECVD) of noble metals has great importance for practical applications in semiconductor industry, protective coatings, electronics, catalyst industries, optoelectronics and refractory ceramic materials. Thin films of noble metals deposited on a substrate surface have high thermal/chemical stability, high electrical conductivity and catalytic activity. Coatings of fully dense morphology developed by CECVD method are necessary to offer effective corrosion/oxidation protection. Thin films of palladium developed by CECVD are of enormous interest in catalysis and microelectronic devices. CECVD is particularly useful for the deposition of thin films on polymer surface due to its low melting point as compared to the glass or silicon [26,135]. Silicon nanowires are prepared by catalyst assisted chemical vapor deposition. Silicon nanowires based solar cells fabricated on stainless steel, have been developed [136]. Yttrium oxide thin films formed by catalyst enhanced chemical vapor deposition have potential applications as electronic insulators, protective coatings, optical or magneto-optical materials and reaction barriers [23]. Catalytic chemical vapor deposition (CCVD) has emerged as one of the most flexible and efficiently attractive technique for the synthesis of single walled as well as multi-walled carbon nanotubes. Nano-sized transition metal particles such as copper, nickel, Cobalt, molybdenum and iron have been successfully

applied as catalysts via CCVD process for the synthesis of carbon nanotubes [53,137].

7. CONCLUSIONS

CVD is a vital process used to produce thin coatings of high purity. The deposition of the films can be performed at considerably lower temperature by applying different types of catalysts. Catalyst Enhanced Chemical Vapor Deposition (CECVD) has emerged as a new enhancement technique. It is particularly suitable for the deposition of metallic films on thermally sensitive substrates. Scientists around the world are successfully applying this method for the production of high quality films of improved purity at low temperature. Palladium, Platinum, and Nickel have been found to be very suitable catalysts for deposition of metallic coatings on polymers. Catalyst nanoparticles play a key role in carbon nanotubes growth by Catalytic chemical vapor deposition (CCVD). CNTs growth via CCVD process include the decomposition of carbon source at the metal catalyst surface through catalytic mechanism, diffusion of carbon into metal catalyst particles and finally the precipitation of solid carbon due to its supersaturation in the catalyst particles. However, this technique has not been fully availed as yet. By the application of suitable nano-catalysts, the CVD temperature can be brought down to room temperature in CNTs growth. Transition metals have been reported to be appropriate catalyst in this process as they are capable of decomposing the hydrocarbons used for CNTs growth. Alloys of these metals have proved to be better catalysts and produce CNTs of high quality. In future, Alloys of trimetals can further improve CNTs growth through CCVD process.

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