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Review Article

Growth of metal oxide thin films by Pulsed laser deposition- Perspectives of Pulsed laser ablation mechanism

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Abstract: A laser is a device that emits light through a process of optical amplification based on the stimulated emission of photons. Pulsed operation of laser refers to any laser not classified as continuous wave, so that the optical power appears in pulses of some duration at some repetition rate. This encompasses a wide range of technologies addressing a number of different motivations. Pulsed laser deposition is a growth technique in which photonic energy is coupled to the bulk starting material via electronic processes. PLD has normally been done with either solid state or excimer lasers producing milli joule to joule pulse energies with 10 kHz to 10 Hz repetition rates, respectively. Solid state batteries using solid-electrolyte have attractive advantages compared to conventional liquid-electrolyte batteries such as lead-acid batteries or nickel-cadmium cells. PLD is a successful thin film deposition method for the preparation of epitaxial oxide films on different single crystalline substrates. The advantage of PLD is the stoichiometric transfer of complex target materials to the substrate, which can be maintained at a high temperature in a reactive atmosphere. Many new devices may be formed using such high quality single crystalline oxide thin films. This paper deals with the detailed technological aspects of PLD, deposition of different thin films using PLD and the advantages of this method.

Keywords: Laser, Ablation, Pulsed laser deposition, Experimental setup, Solid state batteries, thin films and Advantages.

INTRODUCTION

A laser is a device that emits light through a process of optical amplification based on the stimulated emission of photons. The term laser originated as an acronym for Light Amplification by Stimulated Emission of Radiation. The emitted laser light is notable for its high degree of spatial and temporal coherence. Pulsed operation of laser refers to any laser not classified as continuous wave, so that the optical power appears in pulses of some duration at some repetition rate. This encompasses a wide range of technologies addressing a number of different motivations. Some lasers are pulsed simply because they cannot be run in continuous mode. In other cases the application requires the production of pulses having as large an energy as possible. Since the pulse energy is equal to the average power divided by the repetition rate, this goal can sometimes be satisfied by lowering the rate of pulses so that more energy can be built up in between pulses. In laser ablation for example, a small volume of material at the surface of a work piece can be evaporated if it is heated in a very short time, whereas supplying the energy gradually would allow for the heat to be absorbed into the bulk of piece, never attaining a sufficiently high temperature at a particular point[1].

Pulsed laser deposition: Pulsed laser deposition (PLD) is a growth technique in which photonic energy is coupled to the bulk starting material via electronic processes. The principle of PLD is shown in **Fig. 1.**
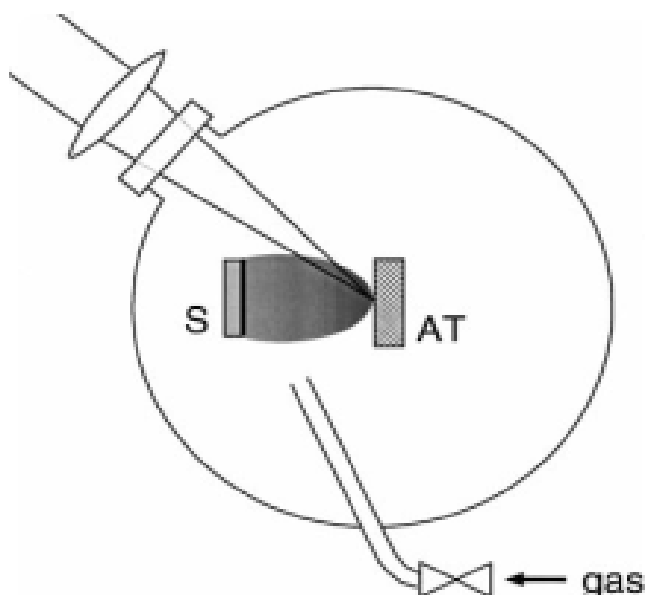

Fig. 1: Principle of pulsed laser deposition

An intense laser pulse passes through an optical window of a vacuum chamber and is focused onto a solid or liquid surface, where it is partially absorbed. Above a certain power density, significant material removal occurs in the form of an ejected luminous plume. The threshold power density needed to produce such a plume depends on the target material, its morphology and the laser pulse wavelength and duration, but might be of the order of 10-500 MW cm^{-2} for ablation using ultraviolet (UV) excimer laser pulses of 10 ns duration. Material from the plume is then allowed to recondense on a substrate, where film growth occurs. The growth process may be supplemented by a passive or reactive gas or ion source, which may affect the ablation plume species in the gas phase or the surface reaction, in which case one talks of reactive PLD[2].

PLD is a thin-film deposition method, which uses short and intensive laser pulses to evaporate target material. The ablated particles escape from the target and condense on the substrate. The deposition process occurs in vacuum chamber to minimize the scattering of the particles. In some cases, however,

reactive gases are used to vary the stoichiometry of the deposit. PLD has offered an interesting alternative for other physical vapor deposition (PVD) methods, because of the low deposition temperature. Most of the PVD methods require the substrate temperature to be at least 300-400°C to achieve a proper adhesion between the substrate and the coating. In PLD, however, it is possible to get an excellent adhesion, although the substrate is at room temperature. So, PLD gives an opportunity to coat heat sensitive materials like polymers, as well[3].

PLD has normally been done with either solid state or excimer lasers producing milli joule to joule pulse energies with 10 kHz to 10 Hz repetition rates, respectively. Pulse widths are in nanosecond range which generally leads to poor quality films with rough morphology and large particle contamination. Such pulses are long enough for heat to conduct away from focal spot. If the pulse length is shorter than electron-phonon relaxation time, the energy lost for heat conduction should be minimized[4]. The onset of vapor and plasma injection or tearing of the target takes tens of picoseconds. This time is the upper limit of pulse length in order to avoid plasma shielding during the pulse. Material emission stops after few hundreds of nanoseconds and within few microseconds time the plasma plume has largely dissipated and no longer reflects the incoming laser beam. This is the lower limit for the time between the pulses in order to ensure that the residual plasma does not reflect the next incoming laser pulse. It is measured that ablation rates with 4 MHz picosecond range pulses are 100 times higher than with nanosecond range pulses and also 10-30 times higher than with 1 kHz femtosecond pulses. Ideally all energy impinging upon the target should be used to generate vapor or plasma in an effective PLD process. By measuring the spectrum of the plasma, one can define the content of atomic species vs. large clusters that produce a black body radiation spectrum. These particles are generated from very dense plasma and molten material[5].

Ablation mechanism: When the laser radiation is absorbed by a solid surface, electromagnetic energy is converted first into electronic excitation and then into thermal, chemical, to cause evaporation, ablation and excitation. Evaporants form a plume consisting of a mixture of energetic species including atoms, molecules, electrons, ions, clusters, micron-sized solid particulates, and molten globules. Under typical PLD experimental conditions, the energy fluence is a few J/cm^2 for 10^{-8} second pulses. This energy is almost one order higher in magnitude of the ablation threshold of most materials. The peak power density under this condition exceeds 10^8 W/cm^2. The electric field inside an absorbing medium under this condition can be estimated from the following relation[6].

$$E = (2\phi/c\varepsilon_0 n)^{1/2}$$

Where E is the electric field, ϕ the power density, ε_0 the dielectric constant in vacuum, n the refractive index of the medium and c the speed of light. For a material with n = 1.5 under a radiation power density of 5 x 10^8 W/cm^2, the corresponding electric field inside the bulk reaches 5 x 10^5 V/cm^2, high enough to cause local dielectric breakdown. Therefore, the molten surface layer vaporizes to form dense plasma. The early stage of plasma flow is hydrodynamic and expands iso-entropically into the vacuum like a supersonic nozzle beam. It absorbs the remaining portion of the laser pulse to reach a higher temperature. Plasma temperature is of about 10^5 K. During the rapid supersonic expansion, a shock wave is generated. Its recoil pressure exerts a force strong enough to ripple the molten surface layer. The oscillatory motion of the ripples propagates along the surface and is interrupted by the liquid-solid interface at the edge of the molten pool. The continuous propagation crashes against the solid interface and expels liquid droplets into vacuum. It is the major cause of "splashing". As the reactive gas pressure increases, so does the frequency of collisions among various species. Multiple collisions take place and promote condensation among molecular and atomic species to form clusters ranging from dimers to submicron clusters. Their density and distribution are sensitive to background gas pressure and the distance from the target surface.

In general, the cluster concentration in the plume increases with background gas pressure and the distance from the target[7].

EXPERIMENTAL SETUP

Fiber laser: We have used a new type of mode-locked fiber laser to achieve optimal laser parameters in PLD. Maximum average power was 20W at 4 MHz. This results in 5 µJ pulse energy. The pulse length was 15-20 ps when measured with a high speed oscilloscope in which gives 250 kW-300 kW peak power. Pulse repetition rate could be varied from 250 kHz to 30 MHz but the maximum pulse energy was kept at 5 µJ while not exceeding the 20W average power. These parameters are commonly found to be best for PLD but so far it has been difficult to find a compact and easy to use laser with such characteristics. In order to reach threshold fluence for the materials studied, we focused the beam into a 15-25 micron spot. This gave maximum fluences of about 4 J/cm^2 at 5 µJ which is more than adequate for the materials studied. During the deposition, the laser beam must be scanned at high speed across the target material. We used a standard galvo-scanner outside vacuum chamber that could scan the beam up to 2 m/s. The range was depended on the focal length of a plano-convex focusing lens. The smallest spot size was reached at a 60 mm focal length resulting in a 20 mm scan length on the target[8].

Vacuum chamber: The fiber laser was connected to the vacuum chamber through a window on the top. The scanner head was attached as close as possible to the window to allow maximum freedom for optimal target and substrate geometry inside the vacuum chamber. The target material was attached to a linearly movable holder that allowed two dimensional scanning in one axis (z-axis) while target was moving in the other (x-axis). During scanning the beam was focused on the target and the incident angle to target was 45 degrees. This setup allowed peeling of the target layer-by-layer from an area defined by scan length in the z-direction and the linear x-movement of target holder. The Substrate holder was also set at a 45 degrees angle to the plume enabling linear movement through the plume that ensured maximal homogeneity of the film.
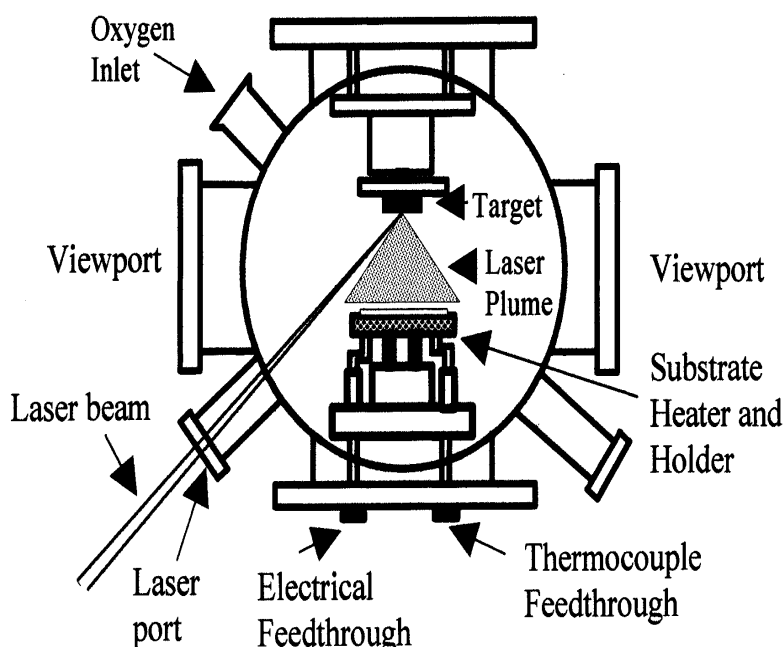

Fig. 2: Schematic diagram of the pulsed laser deposition system

In case of transparent substrates and transparent films, a very simple and effective geometry for the PLD can be used. The transparent polymer or glass substrate can be positioned between the fiber laser scanner and target material since the laser spot size at substrate position is very large compared to focus position

at the target. Thus the fluence at substrate is much below ablation threshold. The orientation of the linearly moving target and substrate can be at a right angle relative to the laser light and its scanning direction. Essentially this means that target material can be transferred layer by layer to the substrate in one to one proportion. Thus roll-to-roll manufacturing is possible for the substrate and in some cases similar rolls can be used for the target materials as well. **Fig. 2** shows the Schematic diagram of the pulsed laser deposition system[9].

SOLID STATE THIN FILM LITHIUM BATTERIES

Solid state batteries using solid-electrolyte have attractive advantages compared to conventional liquid-electrolyte batteries such as lead-acid batteries or nickel-cadmium cells. These advantages include ease of utilization, high reliability, thermal stability, resistance to shocks and vibrations, absence of self-discharge, extremely long active life, absence of possible pollution due to liquid electrolyte, possible miniaturization and possible integration with microcircuits. Rechargeable lithium batteries have received much attention in recent years. There is great interest in the application of solid electrolytes for high performance secondary lithium batteries because of high electrical, chemical and mechanical stability of many lithium compounds. These lithium batteries can be fabricated by successive deposition of contacts, electrodes and an oxide electrolyte. This makes them ideal for integration with microelectronics[10].

Negative electrodes: A number of materials have been used as the negative electrode in lithium batteries, such as lithium, carbon and graphite, lithium-aluminum, lithium-silicon, lithium-tin and intercalation compounds, such as Li_xWO_2, Li_xMoO_2 and Li_xTiS_2.

1) Lithium: Lithium has two unique properties which make it highly suitable as a negative electrode for batteries. Firstly, it is the lightest metal in the periodic table. This is a most attractive property for a lightweight battery. The specific capacity of lithium metal is 3.86 Ah/g. Secondly, lithium has a high electrochemical potential of -3.045 V vs NHE, which holds out the promise of a 3 V battery when combined with a suitable positive electrode. In order to obtain a reasonable cycle life, a three- to fivefold excess of lithium is required. The difficulties associated with the use of metallic lithium stem from its reactivity with the electrolyte and the changes and dendrite formation that occur after repetitive charge discharge cycling. After cycling the surface area of lithium increases with a corresponding increase in the reactivity. This lowers the thermal stability of the system.

2) Carbon materials: The major problem with lithium is the battery safety because of the high reactivity of lithium. Carbon materials can reversibly accept and donate significant amounts of lithium without significant swelling on prolonged cycling. There is no dendrite formation. The usage of carbon and graphite for the negative electrode does not affect the mechanical and electrical properties. The battery becomes safer and is used more efficiently. The chemical potential of a lithiated carbon material is close to that of metallic lithium, thus an electrochemical battery made with a lithiated carbon material will have almost the same open-circuit voltage as one made with metallic lithium. The specific capacity or energy of the lithium ion battery depends largely on the type of carbon materials used, the lithium intercalation efficiency and the irreversible capacity loss associated with the first charge process[11].

Positive electrodes: A variety of materials have been investigated for the positive electrode of lithium batteries, such as intercalation solid compounds, soluble inorganic cathodes and polymeric materials. The best positive electrodes for rechargeable batteries are those where there is little bonding and structural modification of the active materials during the charge and discharge reaction. The intercalation compounds, such as MnO_2, V_2O_5, $LiMnO_2$, $LiVO_2$, $LiCoO_2$, $LiMn_2O_4$ and $LiNiO_2$, are among the most useful positive electrode materials. In these compounds, a guest species such as lithium can be inserted interstitially into the host lattice during discharge and subsequently extracted during recharge. Key

requirements for these compounds for the positive-electrode are: high free energy of reaction with lithium, wide range of the amount of intercalation, little or no structural change on reaction, highly reversible reaction, rapid diffusion of lithium ions in solid, good electronic conductivity, no solubility in electrolyte, readily available or easily synthesized from low cost reactants.

1) LiCoO$_2$: LiCoO$_2$ gives a high capacity 155 mAh/g and cycle numbers. It has a voltage of   4.1 V vs. lithium. It is used in most of the lithium batteries in production in spite of its limited availability and cost. LiCoO$_2$ has a layer structure, where lithium and transition metal cations occupy alternate layers of octahedral sites in a distorted cubic close-packed oxygen-ion lattice. The layered metal oxide framework provides a two dimensional interstitial space, which allows for easy removal of the lithium ions. The dimensional changes on charge-discharge cycling are small. LiCoO$_2$ is the most widely used material for commercial lithium batteries due to its excellent electrochemical cycling stability. It is a result of the structural stability of the material, in which the layered cation ordering is extremely well preserved even after a repeated process of insertion and extraction of Li$^+$ ions. Even though the technology is rather expensive and the material is highly toxic, lithium cobaltate is still the most widely used cathode material in lithium-ion batteries.

2) LiMn$_2$O$_4$: LiMn$_2$O$_4$ has a lower capacity 120 mAh/g but a higher voltage 4.2 V than LiCoO$_2$. It offers an advantage in terms of the availability of natural resources and cost. LiMn$_2$O$_4$ has a spinel or tunnel structure which possesses a three-dimensional space via face sharing octahedral and tetrahedral structures. This provides conducting pathways for the insertion and extraction of lithium ions. LiMn$_2$O$_4$ powder used in lithium batteries is fabricated at high temperatures. However, most semiconductor devices and micro electro-mechanical systems (MEMS) are fabricated at lower temperatures. If we attempt to integrate microbatteries in pre-integrated devices on substrates, the process temperature for microbattery fabrication must be lower than 500^{0}C. Many anode and electrolyte materials, which are synthesized at low or ambient temperatures, have been studied. However, candidate materials for cathode films are almost always deposited at high temperature are introduced during the post annealing process. These materials are not suitable for use as MEMS power sources.

3) LiNiO$_2$: LiNiO$_2$ has a higher capacity 200 mAh/g but a lower voltage 4.0 V than LiCoO$_2$. It has a layer structure. The dimensional changes are small. Despite its high capacity and low cost, LiNiO$_2$ is not widely used commercially because of the energy involved upon decomposition, the relatively low temperature at which self heating ensues and the difficulty of preparing the material consistently in quantity. It is well known that LiMO$_2$ (M = Co, Ni) materials exhibit excellent electrochemical features as cathodes in lithium batteries owing to their layered structure. Particularly LiNiO$_2$ offers some significant advantages when compared to LiCoO$_2$. For instance, LiNiO$_2$ is cheaper and exhibit a higher specific capacity. However, LiNiO$_2$ with the correct stoichiometry is very difficult to obtain.

Solid electrolytes: Ionic transport in solids is related to the atomic disorder in real crystals. The most important defects are vacancies and interstitials. Charged defects have an effect on electronic concentration and accordingly on electronic leakage current. An ionically conducting material may readily turn into an electronic conductor. The most important driving forces for the motion of ionic defects and electrons in solids are the migration in an electric field and the diffusion under the influence of a chemical potential gradient. Depending on the majority charge carriers, quite different driving forces and fluxes apply for the ions and electrons in solid electrolytes and electrodes. The majority carriers are transferred in an electric field whereas the minority charge carriers are moved by diffusion. The solid electrolyte therefore carries the mobile ions according to Ohm's law and the electronic carriers according to Fick's law. The electrodes carry the ions towards the interfaces with the electrolyte by diffusion. The mobility rather than concentration of electrons and holes has to be small in electrolytes. Solid electrolytes for battery applications require high ionic conductivities and wide range of appropriate thermodynamic

stability. Four major aspects should be taken into consideration for the design of suitable solid electrolytes: (i) optimizing the lattice structure spatially and energetically to improve the number and mobility of ionic defects, (ii) developing synthesis routes which lead to materials of amorphous or polycrystalline structure with high overall conductivity, (iii) optimizing the stability range to prevent chemical reactions with the electrodes, (iv) optimizing the electrolytic domain with negligible electronic conduction over the activity range employed. It is difficult to prepare all solid state batteries except possibly thin film batteries with good contacts between the electrolyte and electrodes because of differences in the thermal expansion coefficients of different materials and because of undesirable side reactions at high temperatures. The electrolyte generally used in solid state thin film lithium batteries is lithium phosphorus oxynitride (LiPON). LiPON has a good lithium ion conductivity and excellent stability in contact with metallic lithium. **Fig. 3** shows the schematic representation of Li-ion battery[12].
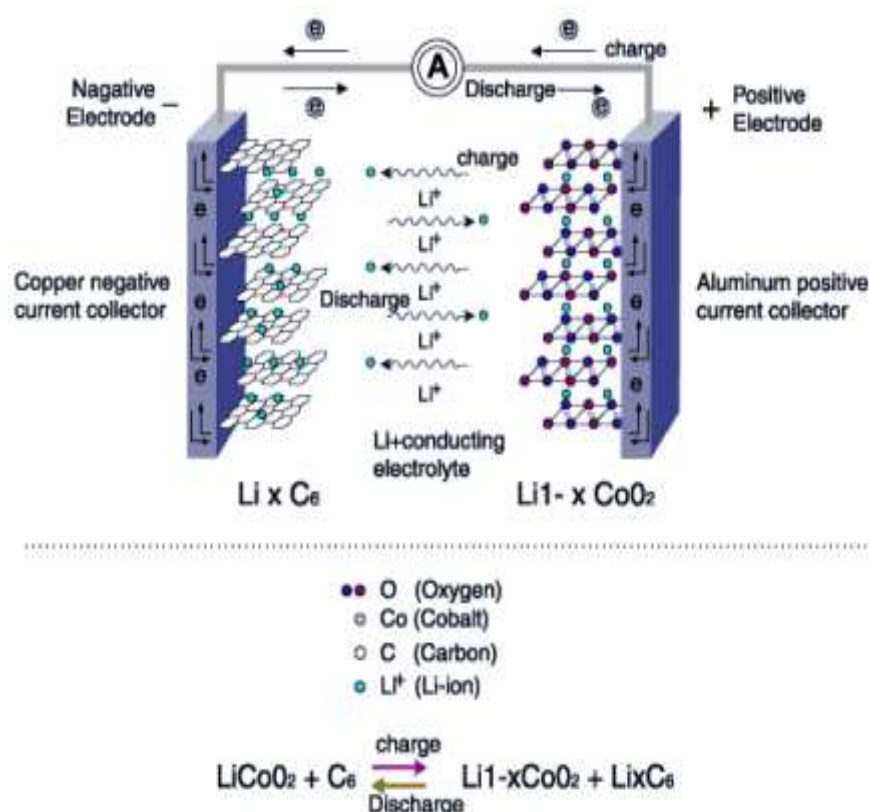

Fig. 3: Schematic representation of Lithium-ion battery

DEPOSITION OF THIN FILMS USING PLD

PLD is a successful thin film deposition method for the preparation of epitaxial oxide films on different single crystalline substrates. The advantage of PLD is the stoichiometric transfer of complex target materials to the substrate, which can be maintained at a high temperature in a reactive atmosphere. Many new devices may be formed using such high quality single crystalline oxide thin films. Low noise high temperature superconductor (HTS) rf-SQUIDs prepared from $YBa_2Cu_3O_{7-x}$ (YBCO), which are used in the nondestructive evaluation of defects in air plane wheels, are just one example for these devices. The improvement of the fabrication yield of these SQUIDs in order to achieve reproducible low 1/f noise performance is a big challenge[13,14].

Growth of LiCoO$_2$ thin films: LiCoO$_2$ is a typical and most commonly used cathode material for rechargeable Li-ion batteries due to its high capacity (136 mAh/g) and good cycling stability. Due in

large parts to this high energy storage capacity, $LiCoO_2$-based rechargeable batteries are now commonly used in high-end consumer electronics such as laptops and cell phones. There is also an increasing interest in fabrication thin film cathodes for application in all-solid-state microbatteries such as for on chip applications[15]. Thin films also received much attention from studying the intrinsic electrochemical properties of lithiated transition metal oxides because no polymer binder and electronically conducting carbonaceous powders exist in thin film cathodes[16]. Thin films of $LiCoO_2$ have been synthesized by a variety of techniques including RF sputtering deposition, low-pressure chemical-vapor deposition, oxidation of Co films in molten carbonate salts and pulsed laser deposition. In the fabrication of $LiCoO_2$ thin films, formation of the layered structure is known to be crucial for obtaining a good rechargeablity of the batteries. PLD is a successful technique in the growth of materials containing volatile components with complex stoichiometry. For this reason, it is well suited to the films of lithiated transitional metal oxides, where lithium loss due to volatilization is a main concern in conventional evaporation methods. The electrochemical behavior of (0 0 3) highly textured $LiCoO_2$ thin films grown by PLD have been investigated[17].

Growth of $LiMn_2O_4$ thin films: Lithiated transition-metal oxides (LTMOs) such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ have received significant attention due to their industrial applications especially in rechargeable lithium-ion batteries [18,19]. These materials are applied on the cathode side where Li is, respectively extracted and stored during the charge-discharge cycle of the battery. It has been reported that the spinel structure $LiMn_2O_4$ exhibits a specific capacity about 120 mAh/g, where composite sample electrodes were used. $LiMn_2O_4$ crystallizes with a spinel structure and belongs to the Fd3m (O_h^7) space group[20] with cubic lattice parameter a=8.239 A . The cubic spinel $LiMn_2O_4$ structure is described with the Mn and Li cations on the 8d and 4a sites, respectively and the oxygen ions on the 32e sites. Half of the octahedral interstices are occupied by the Mn ions forming 3D framework of edge-sharing MnO_6 octahedra. Lithium ions occupy tetrahedral sites, which share common faces with four neighboring empty octahedral sites at the 16c position. Together tetrahedral sites form a three-dimensional network of transport paths 16c-8a-16c through which lithium ions diffuse. Preparation of $LiMn_2O_4$ in thin-film form may have advantages from a point of view of fundamental studies and of the emerging field of microbatteries as well. Thin films of LTMOs have been synthesized by a variety of techniques including sputtering, spray deposition, reaction of metals and pulsed laser deposition[21]. In the fabrication of $LiMn_2O_4$ thin films, formation of the spinel structure is known to be crucial for obtaining a good recharge ability of the cells. Various aspects of $LiMn_2O_4$ thin films prepared by RF sputtering[22], electron beam deposition[23] pyrolytic preparation[24] and pulsed-laser deposition[25,27] have been reported. Thin films of amorphous $LiMn_2O_4$ have been prepared onto substrates maintained at low temperature with reactive electron beam evaporation with RF magnetron sputtering[28].

Fabrication of metal nanoparticle films: The term nanoparticle (NP) usually refers to condensed phase particles with size in the range of 1-100 nm. In recent years there has been much interest in the fabrication and characterization of transition metal and noble metal NPs due to their interesting optical, catalytic, electronic and magnetic properties[29]. For many of these potential applications the NPs need to be deposited on solid substrate. PLD is relatively simple and flexible technique for thin film deposition and nanofabrication. Both nanosecond (ns) and femtosecond (fs) pulsed lasers can be used for the ablation process. For NP growth with ns-PLD, there is much evidence that the NP growth takes place by surface diffusion of deposited material have prepared Pt NPs on highly oriented pyrolithic graphite by ns-PLD [30]. By studying the morphology of NPs at different equivalent thickness they found that the NP size varies with equivalent solid-density thickness. A similar trend has been observed in the fabrication of nano composite films of Cu and amorphous alumina[31]. It is observed that NPs are present in the ablation plume and can be collected on a solid substrate. By studying the ablation plume dynamics using fast photography and optical emission spectroscopy, they have found that the ablation plume has two very

distinct components: a fast atomic plume moving at few km-s^{-1} followed by a NP plume expanding with nearly 10 times smaller velocity[32].
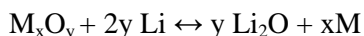
Diamond-like carbon thin films: The use of diamond thin films has the potential for major impact in many industrial and scientific applications. These include heat sinks for electronics, broadband optical sensors, windows, cutting tools, optical coatings, laser diodes, cold cathodes and field emission displays. The attractive properties of natural diamond include physical hardness, high tensile yield strength, chemical inertness, low coefficient of friction, high thermal conductivity and low electrical conductivity. Unfortunately, these properties are not completely realized in the diamond thin films that are currently produced. For diamond film production, high-purity carbon can be ablated directly by lasers and deposited as thin films at ambient temperatures[33]. However, the lasers currently in use generally deliver long pulses and generally explosive nature of laser ablation, in addition to the desired single atom or single-ion carbon, liberates significant amounts of carbon clusters and macroscopic particles of carbon. These carbon particles interrupt the ordered deposition of crystalline diamond, forming undesirable grain boundaries and rough surfaces that are difficult to polish. In addition, PLD generated films that tend to be "amorphous" or nanocrystalline with no observable long range order, but still possessing physical properties which are diamond-like in some approximation. This has given rise to the use of terms such as amorphous diamond, diamond like carbon and recently and more appropriately tetrahedrally bonded amorphous carbon to distinguish these materials from true crystalline diamond. In addition, growth rates for PLD with lasers running typically at a repetition rate of nearly 10 Hz have been prohibitively slow until the recent advent of high-average-power, high- repetition-rate lasers[34].

Vanadium pentoxide thin films: Vanadium pentoxide (V_2O_5) is quite interesting and has been widely studied in recent years in view of its novel material characteristics, which can be readily integrated into many scientific and technological applications. V_2O_5 exhibits electrochromism, photochromism and has high potential for the development of electrochromic devices, electronic information displays and color memory devices[35]. Its ability to incorporate large amounts of lithium ions coupled with its peculiar optical properties ranks vanadium oxides among the most studied materials for electrochemical applications and in particular, for application in solid-state batteries and information displays. V_2O_5 films can also be integrated in other technological applications where the typical functions of these films include chemical sensing, catalysis, optical and electrical switching[36].

Recently, extensive and successful efforts have been undertaken for thin film processing of various vanadium oxides using PLD since it is an attractive choice for the preparation of stoichiometric and high quality metaloxide thin films for various applications. The PLD grown vanadium oxide films have been demonstrated to exhibit enhanced performance when compared with films obtained by other conventional deposition techniques. However, detailed investigation on the fundamental understanding of the growth behavior and surface quality of these pulsed-laser deposited vanadium oxide films has not been made. Understanding the growth and morphological evolution of pulsed-laser deposited vanadium oxide films in relation to the growth conditions would benefit our ability not only to explore the possible technological applications of V_2O_5 films but also to further tune the growth conditions to obtain films with desired characteristics[37].

Nanocrystalline Co_3O_4 thin film electrode for Lithium-ion batteries: Nano-sized 3d transition metal oxides have extensively been investigated for their potential application and new mechanism in lithium ion batteries as anode materials[38]. These transition metal oxide electrode materials exhibited excellent cycle reversibility and high specific capacity. This mechanism involves the reversible formation and decomposition of Li_2O, accompanying the reduction and oxidation of transition metal nanoparticles in the range 1-10 nm respectively. The electrochemically driven nano-size confinement of the metal

particles is believed to enhance their electrochemical reaction activity. The new electrochemical reaction mechanism can be written as

$$M_xO_y + 2y\ Li \leftrightarrow y\ Li_2O + xM$$

Where M is transition metal such as Co, Ni, Fe, Cu etc. Among them, nano-sized Co_3O_4 demonstrated excellent electrochemical property with a specific capacity of nearly 1000 mAh/g, which is about nine times the volumetric capacity of carbon[39]. It should be noted that the lithium insertion process of the Co_3O_4 involves the formation of $Li_xCo_3O_4$ and CoO, which is different from above transition metal oxides with a typical cubic rock salt structure. Furthermore, different electrochemical reaction paths are dependent on the texture of the active material and the discharge rate[40]. Thin films fabrication and characterization of these nano-sized transition metal oxides should be paid attention for its application in all solid state microbatteries. For the fabrication of Co_3O_4 thin film, there are many deposition techniques currently in use but there is no report on the thin film fabrication and electrochemical properties of nano-sized Co_3O_4 prepared by PLD[41].

Lithium nickel oxide thin films: The layered form of lithium nickel oxide $LiNiO_2$ is used as a battery electrode while the cubic form of lithium nickel oxide written as $LixNi_{1-x}O$ may have promising electrochromic performance. $LixNi_{1-x}O$ can have a wide optical range and more neutral color than tungsten oxide as well as better stability. Furthermore $Li_xNi_{1-x}O$ is anodically coloring so it has the advantage of being complementary to cathodic tungsten oxide. The main disadvantage of $Li_xNi_{1-x}O$ is that it is difficult to deposit in the desired composition and phase. The best results were obtained by PLD which has not often been used to deposit electrochromic film[42].

FeSi Thin films: With all its remarkable properties, when used in AC magnetic devices, the industrial iron has two major disadvantages: high electrical conductivity and bad magnetization loops. To reduce such losses and to improve the quality of electrical devices, soft iron must be used in alloys together with other elements; the most important and common of these is silicon (Si). FeSi alloys maintain their magnetic properties up to 33% Si content that corresponds to 50% atomic percentage. These types of alloys are used mainly for the construction of electrical machinery, electrical transformers and in power equipment that works at the industrial AC frequency. Thin films of such alloys are usually developed by PLD[43].

ADVANTAGES OF PLD

There are several advantages of PLD system over other deposition systems. When a multiple-component target is heated on its way to vaporization, individual constituent element segregate in the solid because of their different volatility. Elements with the highest vapour pressure will be vaporized first, followed by the less volatile ones. In other words, the source material does not melt and vaporize congruently and a thin film deposited under this condition does not maintain the target stoichiometry. In PLD, the short thermal cycle induced by laser pulse provides a simple solution to this problem. The volume heated by each pulse is characterized by the laser spot size multiplied by the penetration depth, $L = 2\ (D\tau)^{1/2}$, where D is the thermal diffusivity and τ the laser pulse duration. If L is less than the thickness of material ablated per pulse, then the stoichiometry of the plume will be the same as the target, enabling the use of the single source[44]. This criterion is satisfied by many materials. Simultaneous and sequential evaporation using multiple sources can be easily done by directing the laser beam with external mirrors. PLD has some resemblance to magnetron sputtering. But in the growth of oxide thin films by magnetron sputtering, excessive oxygen causes resputtering whereas insufficient oxygen results in high oxygen deficiency. PLD does not have this short coming. The high plasma temperature of the ablation plume acts as an energy reservoir for activating the reactive background gas. This technique is an ideal to grow thin

films of exotic materials when only a small quantity is available. In addition to oxides, PLD has also been effective in growing nitride films in nitrogen ambient[45], multilayered structures such as superconductors[46] and ferroelectric memory devices [47]. PLD is also known for its fast turnaround time when growing a thin film of a new material starting from its powder form. The ablation species have higher kinetic energy up to a few KeV's and also potential energy in the form of high plasma temperature. In case of reactive deposition, the kinetic energy is retarded by collision to just a few electron volts, which is sufficient to enhance crystallinity. The high plasma temperature of the plume which enhances the reactivity of the gas. Pulsed laser deposition has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films. In particular, it has been successfully employed for the deposition of simple and complex metal oxide materials with desired composition, structure, physical and chemical properties. When PLD is carried-out in the atmosphere of a chemically reactive gas, the flux of the laser ablated material interact with the gas molecules all along the transit from the target to the substrate, as well as on the substrate surface. The resulting deposited layers are found to have the chemical composition considerably the same as that of the starting material. Another chief advantage is, PLD films crystallize at relatively low deposition temperatures than the other physical vapour deposited films. In addition, PLD is environmentally friendly[48].

The technique of PLD was found to have significant benefits over other film deposition methods, including: the capability for stoichiometric transfer of material from target to substrate, i.e. the exact chemical composition of a complex material such as YBCO, can be reproduced in the deposited film, relatively high deposition rates, typically ~100s Å/min, can be achieved at moderate laser fluences, with film thickness controlled in real time by simply turning the laser on and off, the fact that a laser is used as an external energy source results in an extremely clean process without filaments. Thus deposition can occur in both inert and reactive background gases and the use of a carousel, housing a number of target materials, enables multilayer films to be deposited without the need to break vacuum when changing between materials[49].

In addition to superconducting films, PLD of complex ceramic oxides has also been shown to produce high quality ferroelectric, magneto resistive and recent demonstration of colossal magnetoresistivity in films[50] of $La_{0.67} Ca_{0.33} MnO_x$. The most interesting aspect of these developments is that it is now possible to use PLD to combine two or more types of ceramic oxide in heterostructures, enabling novel device applications. In the area of semiconducting films, PLD has been used to deposit a wide range of materials, including SiGe and GaAs-based alloys, II-VI compounds and Group III-Nitrides. Again, the ability to tailor device properties by the growth of heterostructures is interesting, as is the possibility of introducing dopants during growth through the use of controlled pressures of reactive background gas[51].

CONCLUSIONS

Pulsed laser deposition is a thin-film deposition method, which uses short and intensive laser pulses to evaporate target material. The ablated particles escape from the target and condense on the substrate. The deposition process occurs in vacuum chamber to minimize the scattering of the particles. In some cases, however, reactive gases are used to vary the stoichiometry of the deposit. Rechargeable lithium batteries have received much attention in recent years. There is great interest in the application of solid electrolytes for high performance secondary lithium batteries because of high electrical, chemical, and mechanical stability of many lithium compounds. PLD is a successful thin film deposition method for the preparation of epitaxial oxide films on different single crystalline substrates. The technique of PLD was found to have significant benefits over other film deposition methods, including: the capability for stoichiometric transfer of material from target to substrate, i.e. the exact chemical composition of a

complex material such as YBCO, can be reproduced in the deposited film, relatively high deposition rates.

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