LOW PRESSURE MOCVD OF COPPER BASED COMPOUNDS FOR PHOTOVOLTAIC APPLICATIONS

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ABSTRACT - In recent years copper based compounds such as copper indium diselenide (CuInSe_2 , CIS) have emerged as the most promising candidates for high efficiency stable solar cells. To date research has been centred around the standard thin film deposition techniques i.e. evaporation, sputtering and electroplating. While these techniques give good films it has proved difficult to gain reproducible results. The production of devices based on CIS thin films has now progressed to a point where, to achieve further advances in device efficiency, more research into alternative deposition techniques and the basic deposition parameters is required. The major problems encountered with the standard technique are poor step coverage and lack of control over the stoichiometry. A low pressure MOCVD reactor has been constructed to investigate the growth of thin film CIS and the factors affecting deposition. The considerations involved in the design of such a system are discussed. A detailed study of reactor parameters affecting low pressure MOCVD of copper, copper indium and copper indium diselenide is being carried out. Mass spectrometric analysis of the decomposition products has been undertaken and the growth mechanisms and kinetics involved in these deposition processes are being investigated.

INTRODUCTION

Over the past few years a great deal of effort has been employed on research into ternary and quaternary compound semiconductors. Two compounds namely Copper Indium Diselenide (CIS) and Copper Gallium Indium Diselenide (CGIS) have shown excellent solar cells properties [1]. A thin film CGIS based solar cell has been produced with an efficiency of >15%, a world record for a thin film photovoltaic device.

To date CIS/CGIS research has been centred around the standard thin film deposition techniques i.e. evaporation, sputtering and electroplating. While these techniques give reasonable films it has proved difficult to gain reproducible results. The production of devices based on CIS and CGIS thin films has now progressed to a point where, to achieve further advances in device efficiency, more research into an alternative deposition technique is required. This technique must allow for accurate control and lead to a fundamental understanding of the electro/opto thin film properties. The production of CIS and CGIS thin film devices has, in the past, often included empirical processing stages in order to optimise efficiencies. Here we mainly refer to the control and identification of intrinsic lattice defects which dominate the bulk and surface properties of the near stoichiometric compositions. These influence a wide range of parameters including lifetime and conductivity type.

The application of chemical vapour deposition (CVD) processes to the production of large area CIS and CIGS thin-films is largely a new development in this field with very little published material available. CVD is generally acknowledged to be ideally suited to large area/throughput processing, particularly with reference to the degree of control which can be obtained over the reproducibility of the properties of deposited films.

The CVD of a ternary or multinary compound can be a complex task. Therefore the initial objectives of this investigation are to consider the deposition of the constituent elements. A great deal of work has been documented on the CVD of compounds containing indium and selenium. It is widely known that trimethyl indium and gaseous hydrogen selenide are suitable precursors for indium and selenium respectively. The CVD of copper is not such a well documented process. It was felt that the initial phase of the work should take the form of a detailed investigation of the precursors, parameters and processes involved in the CVD of thin film copper.

THE CHEMICAL VAPOUR DEPOSITION OF COPPER

The CVD of copper has attracted a lot of attention due to the multiplicity of applications. Work reported in the literature reflects the varying areas of technology to which thin film copper deposition is of interest.

One of the most important areas of research has been the application of CVD to the growth of thin film superconducting alloys [2-4]. A detailed consideration of the copper film growth processes was not undertaken as the interest was in the alloy rather than in its constituents. This approach is in contrast to our investigation, where a deeper understanding of the deposition processes is being sought which will be propitious to the CVD of CIS and CIGS.

Several groups are working on the CVD of thin film copper to develop new metallisation processes for microelectronic device fabrication [5-12]. As demand grows for the miniaturisation of feature size in VLSI technology, so does the need for a highly resolved metallisation process. It is widely hoped that the development of a direct writing CVD technique, obviating the lithographic stages, will give the required improvement in resolution. The activation of such a CVD process is best done by laser means. This technique allows selective writing of the films with high precision. Workers in this field have, however, encountered problems with film (or in this case line) uniformity [5], which appears to be related to the non-uniform temperature profile of the laser beam. Publications relating to the photolytic CVD of copper report carbon contamination, as high as 90 at% in extreme cases. Limited mechanistic studies have suggested that the process proceeds via a photolytic rather than pyrolytic process [6]. It is also reported that difficulties were encountered with the temperature control of the deposition region, and hence detailed study of the effect of substrate temperature on film quality were not investigated in detail.

The majority of publications report the use of various forms of copper hexafluoroacetylacetonate (hfa) as the main precursor. This compound has proved popular due to its low toxicity, solubility in organic solvents and low decomposition temperature (230°C).

Temple and Reisman reported the lack of published work on thermally activated copper CVD in 1989 [13]. In particular they state that no data has been given on the reproducible preparation of copper films with control over properties such as resistivity and uniformity. The growth of films from liquid $\text{Cu}(\text{hfa})_2$, decomposed thermally to give copper, suggests that a simple pyrolysis procedure can break the ligand bond, leaving copper on the substrate. Workers in the field of photolytic CVD have considered a reaction

mechanism system which requires the presence of a hydrogen species to reduce the ligand, facilitating separation from the copper ion [6]. An investigation into plasma enhanced CVD of copper from Cu(hfa)_2 [14] has also suggested that the presence of hydrogen is essential for metallic as opposed to polymeric film growth.

The indication from the literature available is that a full understanding of the reaction mechanisms, along with quantitative analysis of film quality/properties related to changes in the various process parameters, is required in order to yield controlled reproducible films.

We have designed and constructed a flexible CVD system to investigate the deposition of copper as a prerequisite to the deposition of CIS/CIGS, initially from Cu(hfa)_2 . Accurate control is provided over the numerous process parameters which may affect film growth and quality. The system has the ability to vary the temperature of both precursor vaporisers and to provide excellent control over substrate temperature. The reaction chamber pressure can be varied as can carrier and diluent gas flow rates. Gaseous or metalorganic precursors can be injected directly to the reaction site if required, or mixed prior to entering the chamber in a manifold inlet. The system is fitted with an in situ quadrupole mass spectrometric facility allowing the composition of reactant and/or exhaust gases to be analysed, giving vital information about precursor decomposition processes and reaction mechanisms.

CVD SYSTEM DESIGN

It was decided that a modular strategy was the most flexible, allowing easy modification and maintenance. Figure 1.

Figure 1 Schematic of MOCVD System

Gas handling system

The gas handling system consists of three Brooks 5850 mass flow controllers, various pneumatic valves and a pressure monitoring system. The precursor delivery apparatus includes specially designed precursor bottles heated in a thermostatically controlled oil bath, which can reach temperatures of greater than 180°C , far above the melting point of Cu(hfa)_2 . The entire precursor bottle can be immersed to avoid cold spotting.

Reactor

The reactor is a 25cm necked quartz tube of 64mm outside diameter with a stainless steel door assembly. The sliding stainless steel door, containing thermocouple and mass spectrometer feeds, is designed to allow quick loading and unloading of samples making it possible to do a number of depositions in a very short time. The substrates are mounted on a graphite susceptor which sits on a quartz paddle, and are heated using an infra red 1kW Research Inc radiant heater. This water cooled lamp allows the susceptor to be taken to temperatures in excess of 900°C within 5 minutes, whilst the reactor walls remain cool (< 50°C). The lamp is controlled by a Eurotherm 818P programmable temperature controller, regulating to $\pm 0.5^\circ\text{C}$. The in situ annealing of as grown films (without breaking vacuum) is an added advantage.

Vacuum system and mass spectrometer

The chamber is exhausted by a rotary and diffusion pump combination with built in pressure control allowing depositions to be performed over a range of pressures - atmosphere to better than 10^{-6} torr. The CVD system is interfaced to a VG SX300 quadrupole mass spectrometer and computer for data acquisition and analysis. Hence a detailed, real time, in situ analysis of the decomposition processes can be performed.

Control system

The entire system is controlled via a programmable logic controller (PLC) which drives the electronics for all of the transducers, valves, pumps and heaters (including the lamp). The inputs and outputs of the PLC can be sequenced in real time allowing a number of predetermined steps to be combined to formulate the process cycle. Various safety interlocks are checked by the PLC, failure of any of these interlocks automatically places the CVD apparatus into a safe state.

The modular approach to our design and our desire for flexibility has allowed the design of a retrofit plasma enhanced option. This module fits into the existing system, producing a capacitively coupled glow discharge option. This will allow comparisons to be made between plasma enhanced MOCVD and standard MOCVD, while keeping the reactor geometry and gas handling systems unchanged. Results of this work will follow in subsequent correspondence.

EXPERIMENTAL PROCEDURE

Initial work has made use of $\text{Cu}(\text{hfa})_2 \cdot \text{H}_2\text{O}$ in both solid and solvated forms.

A series of depositions were carried out using nitrogen as a carrier gas flowing at 10sccm. A solution of 0.5g $\text{Cu}(\text{hfa})_2$ in 50 cc ethanol, at room temperature (ca 20°C), was used to deposit copper films on to glass substrates at temperatures (T_s) in the range 300-450°C. The effect of change of precursor temperature on film growth rate was investigated. This was repeated using solutions of ethanol and propanol as solvents. Depositions were also carried out using the solid precursor at various temperatures and constant T_s (350°C). All depositions were carried out at a pressure of approximately 20mbar.

An alternative approach to the transport of the precursor was attempted. Carrier gas was bubbled through pure ethanol, heated to 30°C . Ethanol "picked up" by the nitrogen was then passed through solid $\text{Cu}(\text{hfa})_2 \cdot \text{H}_2\text{O}$ placed in the path of the carrier gas/solvent mixture. This technique was employed with flow rates of 5, 10, 15 and 20 sccm nitrogen, with a diluent gas (nitrogen) added such that the total

nitrogen flow rate was held at 50sccm. Films were deposited at 20mbar pressure with a substrate temperature of 350°C.

INITIAL RESULTS AND DISCUSSION

Initial work on the deposition of copper has yielded thin films, successfully grown, by all of the above mentioned techniques.

Use of the solid precursor has so far proved difficult to control since the rate at which the precursor sublimates increases rapidly over a small range of temperature (a few degrees). Heating of the path to the susceptor was required to avoid condensation at cold spots. The films that were obtained by this method were non-uniform, with deposition occurring randomly across the substrate. Fluctuation of the precursor vapour pressure during the deposition was considered a likely cause. This led to the use of solvated forms of the precursor.

For the depositions using the precursor dissolved in ethanol, at room temperature, it was found that growth rate appeared to be largely unaffected by the substrate temperature (300-450°C). Very thin deposits, of the order of 1000Å, were observed for all substrate temperatures after a 30 min deposition. It is thought that the transport of precursor molecules to the substrate was low. The deposition rate was greatly increased for an ethanol/Cu(hfa)₂ solution held at 35°C, supporting the idea that the controlling parameter in this series of experiments is the low vapour pressure of Cu(hfa)₂ in ethanol. Further increase in growth rate was observed for a propanol/Cu(hfa)₂ solution, held at 50°C. A higher solubility of the Cu(hfa)₂ in propanol, as opposed to in ethanol, would partially explain this but an increase of the precursor partial pressure is a more likely cause, since the compound appears to dissolve completely in both solvents. Exact solubility data is not yet available.

The second method of solvent pick up (using pure solvent flowing through solid Cu(hfa)₂) yielded very thin films. The concentration of precursor molecules at the substrate is small when compared to the previous experiments, hence reducing the deposition rate. Work in the literature [10] reports a relationship between flow rates and the amount of precursor transpired (carried to the reaction site). The data presented to support this theory is far from conclusive. Film thicknesses do not appear to follow any obvious relationship to gas flow rate. This is consistent with other work in which attempts to analyse the dependence of "pick up" on flow rate have been made [15]. Controlling all the various parameters that affect the precursor pick up has proved to be difficult. We surmise that there is a dependence on solubility factor, velocity of the carrier gas, amount of precursor left in the tube, gas temperature and system geometry.

Copper films, grown utilising a solvent to transport the precursor had a much brighter, metallic appearance. We surmise that the presence of the solvent effects the overall chemistry of the system as well as assisting the physical transport of the precursor to the substrate. This is in accordance with early work [16] based on hydrogen reduction of Cu(hfa)₂ to produce copper films. More recent work [6] has proposed that decomposition proceeds via the reduction of the copper and the formation of the hexafluoroacetylacetonyl free radical. It is suggested that a species with labile hydrogen atoms (for example an alcohol) can reduce the free radical to stable hexafluoroacetylacetone before reoxidation can occur by the copper ion. Further reduction of the copper to the zero valency state can then proceed.

It was found that the copper films adhered weakly to the glass substrates. The deposits being easily removed. Secondary deposits formed on the quartz paddle, supporting the susceptor, bonded very well.

The bright copper deposit could not be removed by mechanical scraping.

CONCLUSIONS

The deposition of copper films by MOCVD has not been widely investigated. There is a lack of firm understanding of decomposition processes involved and of the effects that the various process parameters have on the reaction kinetics, mass transport and ultimately film quality. Such an understanding is required if reproducible copper films are to be grown with required properties (thickness, resistivity), or if copper is to be introduced in stoichiometric proportions to multinary semiconductors, notably copper indium/gallium diselenide.

A flexible MOCVD system has been designed and constructed to carry out this investigation. Initial work has made use of copper hexafluoroacetylacetonate monohydrate as the precursor. These experiments have shown that copper films can be successfully grown by pyrolytic decomposition of the aforementioned precursor. Films grown so far have been very thin, with growth rates of the order of $<25 \text{ \AA}/\text{min}$.

Initial depositions have shown significant variations in growth rate due to changes in vapour pressure of the precursor. Use of the precursor in the solid form is possible, however control of the sublimation rate is difficult, especially under LPCVD conditions. Film growth rate and quality have been improved by dissolving the precursor in an organic solvent. Precursor transport has been achieved by bubbling nitrogen through the solution and by passing a nitrogen/ethanol mixture over solid $\text{Cu}(\text{hfa})_2$, the latter greatly reducing the growth rate. At reaction chamber pressures around 20mbar the best growth conditions observed so far have been for a $\text{Cu}(\text{hfa})_2$ /propanol solution held at 50°C .

Our investigations are continuing, to ascertain methods of precursor transport in order to control film growth rate accurately. Further experiments are being carried out to investigate the effect of chamber pressure and substrate temperature on film growth rate, composition, crystallinity and electrical properties. When a satisfactory regime has been established a more detailed investigation of the decomposition processes will be carried using in situ mass spectrometry. The effect of substrate temperature, gas mixture, pressure, flow rates and reducing agents on the reaction mechanisms will be investigated to give a full analysis of the process.

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