2．「太陽電池用半導体カーボン薄膜に関する研究」

Chapter 1

General Introduction

1.1 Background

With the advent of modern era, human beings become more dependent on energy while energy reserves are decreasing day by day with increasing rates, which initiates people to realize that the traditional fossil fuels, such as, coal, oil, natural gas are not only limited, but they also contribute to the unpredictable and probably irreversible climate changes in the near future through carbon dioxide (CO_2) and enhances the greenhouse effect. The increasing concern for environmental pollution problems in developed countries has also discredited the nuclear power as a long term energy concept.

The radiative energy output from the sun generates by nuclear fusion reaction while conversion from hydrogen to helium takes place and net mass loss of $4X10^3$ Kg/sec is observed and a huge ($4X10^{20}$J) amount of energy is emitted in every second [1]. Over a year, this corresponds to a figure more than 2000 times (considering all losses and usage in different purposes) the current energy requirements of the human need, while at the same time, fossil fuel reserve will last only for about 37 years (calculation based on assuming that everyone in the world consumes energy at the current rate exhibited by citizen of the United States) [2]. From this perspective, the use of sunlight offer a conceivable alternative to worldwide energy problems. Among the various solar energy converters, photovoltaic (PV) cells are the most extensively studied and well known for their space application (due to availability of sunlight continuously). Table 1.1 [2] lists the principal energy sources currently being utilized by mankind, which gives the picture of fossil fuel consumption rate with respect to other energy sources, though the availability of energy from sun is many times higher than other energy resources, its higher generation cost makes use of solar energy converter, such as photovoltaic (PV) solar cell for mass generation of electricity for common consumer unrealistic. According to the National Association of Regulatory Utility Commissioners (NARUC) [3] the kWh cost of electricity generation by coal-fired steam system is $0.08, for gas/combined cycle system is $0.08 and by PV is $0.24.

2.1 Solar Cell Materials and Prospect of Carbon

Considering all those factors discussed above, recently many scientists [4-6] have been working to develop high efficiency solar cell with the ultimate aim to low down the per unit cost of energy and make it comparable with energy generated from conventional energy sources. Table 1.2 [7-9] shows various types of solar cells including the structure and latest reported highest efficiency. Efficiencies of some solar cells are quite high, such as, single crystal silicon (c-Si) solar cells has efficiency about 24.4%, however, are very expensive. Though, amorphous Si (a-Si) based solar cells are cheap but efficiency is low. Moreover, a major drawback of the a-Si technology is the degradation of the devices under illumination [10]. On the other side, CdTe based solar cell is environmentally hazardous while deposition method of $CuInSe_2$ is very expensive. With respect to present nigh efficient solar cell materials, carbon is a material of highly stable, cheap, non-toxic which can be obtained from precursors those are sufficiently available in nature. Yu et al. [11] had reported highest efficiency of 6.45% from carbonaceous film/n-Si solar cell obtained from 2,5-dimethyl-p-benzoquinone by CVD process. Recently, our group also obtained 2.07 % efficiency from ion beam sputtered phosphorous-doped camphoric-C/ p-Si solar cell [12]. Camphor is a cheap, non-toxic, naturally available material. The result of Yu et al.[11], along with camphoric carbon solar cell result of our group [12-14], prompt carbon material to be one of the future scope of high efficiency, pollution free and one of the cheapest solar cell which can become commercially competitive with present conventional energy sources.

Table 1.1

Energy source contributions to the global energy needs

Energy Source	Current contribution to energy used (%)	Total (%)
Fossil Fuels		
--Coal	25.7	
--Oil	37.6	83.0
--Natural gas	19.7	
Nuclear		
--Fission	5.5	5.5
--Fusion	0.0	
Geothermal	0.1	0.1
Hydropower		
--Dams	5.8	5.9
--Tidal	0.1	
Biological		
--Wood	3.2	3.4
--Other	0.2	
Solar		
--Wind	0.2	2.1
--Thermal	1.8	
--Electrical	0.1	

Table 1.2

Best reported efficiency of some relatively cheap solar cells

Material	Structure	Efficiency (%)
Single crystal Si		24.4
Poly crystal Si		19.8
amorphous Si		13
$CuInSe_2$	$ZnO/Cu(InGa)Se_2$	17.6
	CdS/CuInSe	8.1
CdTe	CdS/CdTe	15.8
CdS	CdS/Cu_2S	10
TiO_2	TiO_2/Dye	13
Carbon	C/n-Si	6.45

1.3 Purpose and Organization of this Dissertation

The objective of this research is to develop a low cost, pollution free solar cell from carbon, as an interesting material, abundantly available in nature. The property of carbon films strongly depends on precursor material and method of its deposition, which will be described in the later chapters in detail. To get the suitable carbon films for the application in optoelectronic devices, camphor ($C_{10}H_{16}O$), a natural source has been used as a precursor. Mostly graphite is used as a solid target for ion beam sputtering and pulsed laser ablation [15-19]. Camphor has hydrogen atoms and also mixture of sp^2 and sp^3 bonded carbon in its structure while graphite has only sp^2 bonded carbon without any hydrogen. Therefore, properties of the carbon films obtained from camphor are expected to be different from that of graphite and may be better in quality. The chemical structure of camphor molecule is shown in Fig. 1.1. In this thesis, various properties of thin film of camphoric carbon deposited by ion beam sputtering and pulsed laser ablation have been studied in order to see the application of this material in high efficiency solar cells in the near future.

In the following chapter (Chap 2), various forms of carbon are described and also present status of amorphous and diamondlike carbon research is reviewed.

Camphoric carbon soot is palletized and has been used for depositing carbon films by ion beam sputtering (IBS) and pulsed laser deposition (PLD) method. In chapter 3, detail of the set up which is made for burning camphor has been presented. The palletized camphoric carbon soot has been used for depositing carbon films by ion beam sputtering method. The films are heat treated in nitrogen ambient at different temperatures and its optical and electrical and structural properties of as-deposited and heat treated films are characterized and reported. As-deposited films have shown 0.5eV optical gap which is observed to be almost constant up to 400℃ heat treatment and decreases rapidly at higher heat treatment temperatures and the films have shown similar behavior to that of hydrogenated amorphous carbon. Analyses of the electrical conductivity have shown the conduction mechanism to be dominated by variable range hopping. In this chapter, detailed analyses of Raman scattering is also reported. The width and position of D-line and G-line as a function of heat treatment temperature is observed to be related to change of the bond angle disorder and structure of the camphoric carbon film. A logical analysis is presented for D-line shift as a function of heat treatment temperature for the first time.

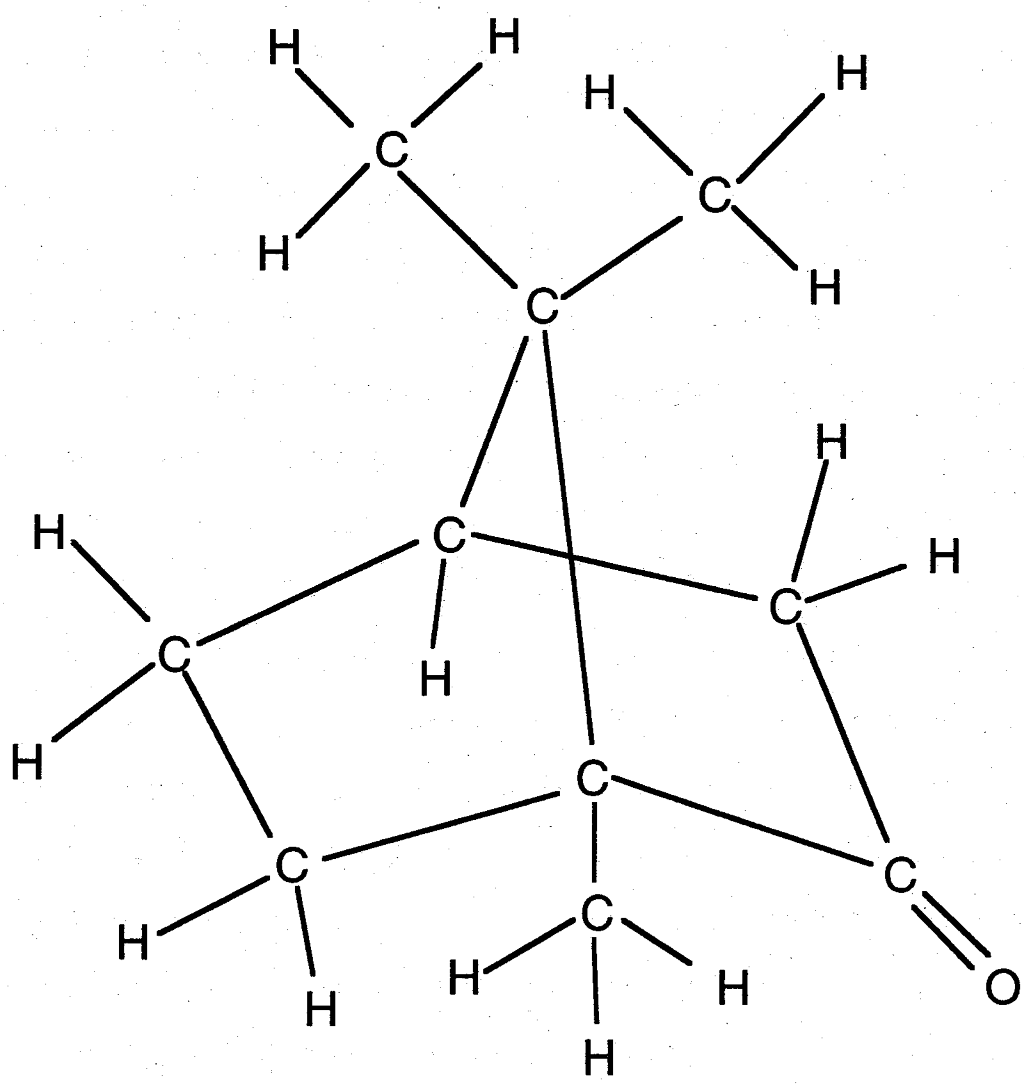

Figure 1.1. Chemical structure of the starting material, camphor ($C_{10}H_{16}O$)

Nowadays, various methods are used for the preparation of carbon films. In fact, the energy of the carbon species generated by various preparation methods is different and plays an important role in controlling the sp^3/sp^2 ratio. In the past decade, pulsed laser deposition (PLD) process has become popular for its ability to generate highly energetic carbon species which enhances the formation of high percentage of sp^3 bonded carbon atoms at low substrate temperatures, and therefore, deposition of high quality of DLC film can be realized. In spite of adequate distinct advantages, the low deposition rate hinders commercialization and restricts the PLD process to the sophisticated research areas only. Moreover, graphite is being used almost exclusively as the target material for physical vapor deposition of DLC films systems, such as, sputtering, filtered cathodic vacuum arc (FCVA), PLD etc. In chapter 4, we present the deposition of DLC films from camphoric carbon target (CCT) by PLD, and compare the results with those of DLC films obtained from conventional graphite target (GT) in search of new target material with more desirable performance.

Microstructure in carbon is complicated due to the presence of both σ and π states. However, undoped carbon is reported to be weakly p-type [16] and presence of the high density of intrinsic defects restricts its successful doping which is the main barrier for its application in various electronic devices. Effective doping can modify electronic properties, specially gap states, conductivity, etc. in semiconductor materials. We have investigated the effect of phosphorus (P) incorporation in DLC films by PLD using CC target and the successful doping is presented in chapter 5.

With the introduction of nitrogen in the area of carbon research, the scope of carbon has widened. Since nitrogen has smaller atomic radius compared to that of phosphorus and is close to that of carbon, the former would be preferred. Further, the nitrogen, being gas phase has the advantage of better control of dopant concentration over phosphorus in physical deposition systems. In chapter 6, we have presented successful doping of nitrogen and carbon nitride (a-C:N) alloy formation by introducing nitrogen gas (N_2) in the PLD chamber.

In chapter 7, photovoltaic cell of P-doped CC/ p-Si heterostructure prepared by PLD using camphor, is presented. Some photovoltaic properties of this heterostructure is studied in dark and under illumination. Effect of P content in the carbonaceous layer also investigated and has suggested the possibility of the low cost, non-toxic carbon based solar cells in the near future.

Finally, a summary and few remarks on the future scope of this dissertation is presented in chapter 8.

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Chapter 2

Carbon Materials

2.1 Introduction

Carbon based materials, clusters and molecules are unique in many ways and allotropes of carbon are inter convertible to each other under suitable temperature and pressure [1]. Under ambient conditions, the graphite phase with strong in-plane trigonal bonding is a stable phase. Under high pressure (60000 atms) and temperature (2000K) graphite can be converted to diamond and when exposed to irradiation or heat, diamond will quickly transform back to the more stable graphite phase. During thin film formation of diamond, it is observed that under a very special condition diamond is formed, otherwise graphite structure predominates.

Carbon has atomic number of 6 and is classified in group IV of the second period of the periodic table and has $1s^2 2s^2 2p_x^1 p_y^1$ electronic ground state configuration. In the graphite structure, strong in plane bonds are formed which is denoted by trihedral sp^2 and in diamond structure, they are tetrahedrally bonded sp^3 configuration.

In this chapter, some major forms of carbon have been described. Furthermore, present status of semiconducting carbon, its application in microelectronic devices and solar cells are described in brief.

2.2 Forms of Carbon

Before the discovery of fullerenes [2], graphite and diamond were known to be the two main allotropic forms of carbon. Graphite has 100% sp^2 structure while diamond has all sp^3 bonded structure. Some important forms of carbon, such as glassy carbon, carbon fiber and carbon blacks have mostly disordered sp^2 bonded structure while diamondlike carbon (DLC), amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) have mixture of sp^2 and sp^3 bonded carbon of different fractions. However, with the introduction of nitrogen (N) in the area of carbon research, the scope of carbon has multiplied.

Soon after the discovery of fullerene family in 1985 by Kroto et al.[2] and nanotubules by Iijima et al. [3], research on carbon and carbon related materials, mainly a-C or a-C:H entered into a new era and scientists all over the world working on this remarkable element, carbon, for its use in opto-electronic devices.

2.3 Carbon Research Background

Amorphous carbon refers to a network of carbon that has both sp^2 and sp^3 bonding and almost no sp^1 bonds [4]. Recently, a lot of researchers have shown much interest in developing microelectronic devices from DLC and a-C films [5-19]. Some characteristic properties of a-C films prepared from various methods are summarized in Table 2.1 [20-48]. Properties of DLC, a-C or a-C:H can have variable band gap from 0.0 eV (metal) to 5.5 eV (insulator), which along with other properties depend strongly on the growth conditions, method of deposition [20, 27, 30, 33] and precursors [41]. Observations from literature showing that the semiconducting carbon films can be either intrinsic [8, 9, 11] or they can be doped during [10-12] or after [9, 13] the growth to make them extrinsic semiconductors. Schottky diodes [12], Metal-insulator semiconductor (MIS) diodes [13] and heterojunction devices on silicon, such as solar cells and thin film transistors (TFT) have been reported [15, 16, 18-20].

Photoconductivity is observed by Amaratunga et al. [17] from tetrahedral a-C (ta-C) deposited by filtered cathodic vacuum arc technique. Under light their film conductivity increased by 2 orders of magnitude.

Nitrogen incorporation in carbon film is reported by many researchers [49-71]. The motivation behind this attempt can be divided into two broad categories; synthesis of crystalline carbon nitride alloy (C_3N_4) and doping of carbon in order to convert undoped p-type carbon to n-type. The properties of crystalline phase of carbon nitride (CN) alloy was reported by Liu and Cohen [57-58]. They have proposed β-C_3N_4, a form of CN alloy, analogous to β-Si_3N_4, should have hardness closer to diamond, a super hard material. Amorphous carbon nitride (a-C:N) already has shown considerable interest in the field of protective coating for magnetic and optical materials [59]. Further, the ability to dope [62] using nitrogen gas has shown a new direction for the application of the carbonaceous material in electronic devices. At present, there are numerous reports of attempts to use nitrogen gas and ion as a doping source. Recently Nitta et al [60] has reported photoconductivity from amorphous-CN_x films which is encouraging for its application in optoelectronic devices in the future.

More encouraging results here reported by Yu et al.[18] of 6.45% efficiency from carbonaceous film/n-Si solar cell and the carbon film was deposited from 2,5-dimethyl-p-benzoquinone by CVD process. However, precursors and method of deposition of carbon films are the two major constraints in order to obtain the required optical and electrical properties for their application in various optoelectronic devices. Hence, an alternative precursor material and simple method of deposition are very much foreseen for better opto-electrical characteristics of carbon thin films.

In this research, camphor has been found as a new precursor material for the deposition of carbon thin films for future opto-electronic applications. It has been reported that camphor has both C and H and moreover, it has both sp^2 and sp^3 carbons in its structure. Also, it is reported that fullerenes [72], carbon tubules [73] and semiconducting carbon [74] have been successfully generated from the soot of this natural precursor, camphor. Based on those reports, it is thought that, camphoric carbon thin films may be different to that of those films obtained from other sources in their opto-electrical characteristics.

Table 2.1

Summery of some important properties of carbon thin films obtained from different methods and precursors

Method of Deposition	Source	Dopants	Band gap (eV)	Thickness (mm)	Conductivity $W^{-1}cm^{-1}$	References
r.f.-PECVD	CH_4,He/C_6H_6 CH_4,Ar C_4H_6, H_2, Ar	N_2	0.5 - 2.0 1.2 - 4.0	0.4-0.7 8/nr	— 10^{-12} - 10^{-6}	20 - 26
r.f.-Glow Discharge	CH4, C2H6, C2H4, C2H2	PH3,B2H6,N2	0.5 - 2.6	0.1-2.5	10^{-13} - 10^{-1}	27 - 28
d.c.-Glow Discharge	C6H6, Ar C2H2	N2 PH3,B2H6	0.0 -2.2 0.9 -2.1	0.4 - 2.0 0.1 - 1.0	10^{-8} - 10^{-4} 10^{-16} - 10^{-10}	29 - 32
RF/DC-Magnetron Sputtering	Graphite, Ar, H2		0.5 -1.46	0.5	10^{-10} - 10^{-2}	33 - 34
Filtered-CV-ARC-deposition	Graphite	N2, P	1.8 -2.5	0.1 - 0.3	10^{-9} - 10^{-2}	35 - 36
Ion Beam Deposition	C6H6, CH4		1.0 -2.0	0.6		37 - 38
CVD	C6H6,C5H5N, 2,5,-dimethyl, p-benzoquinone	BCl3	1.6, 1.1 0.25	0.2/hr 0.04	10^{-5} - 10^{0} 10^{-4} - 10^{3}	39 - 41
Ion Beam Sputtering	Graphite, Ar/H2 Camphor, Ar	B, P	<1.0 0.5 -1.5	1-5nm/hr	10^{-7} - 10^{2}	42
Laser Ablation Pulsed-Laser-Arc-Deposition	Graphite, H2		0 -1.9	0.1	10^{-6} - 10^{2}	43 - 45
Micro Wave PECVD	CH4, C2H4, Ar/CH4		1 -2.5	25nm/min 0.5 - 3.0		46 - 48

2.4 Conclusions

Semiconducting carbon research shows the potentiality of the carbon material to be high, especially in opto-electronic applications. In order to obtain suitable opto-electrical properties of carbon thin films for their application in electronic devices, either an alternative precursor or modification of the existing systems are very much needed. Camphor has been chosen as an alternative precursor. In the following chapter, the optoelectrical and structural properties of ion beam sputtered carbon thin films obtained from camphoric carbon soot target is presented. The heat treatment effects of these films are also investigated.

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