Introduction

Recent developments have allowed silicon (Si) semiconductor technology to approach the theoretical limits of the Si material; however, power device requirements for many utility applications of power electronics are at a point that the present Si-based power devices cannot handle high power. The requirements include higher blocking voltages, switching frequencies, efficiency, and reliability. To overcome this limitation, new semiconductor materials for power device applications are needed. Wide bandgap semiconductors like silicon carbide (SiC), gallium nitride (GaN), diamond, with their superior electrical properties are likely candidates to replace Si in the near future for high power, high temperature and harsh environment requirements [Bha 93] [Pet 99] [Ned 02] [Cha 04]. Diamond has the best electrical and thermal properties when all wide bandgap semiconductors are compared [May 00] [Wer 98].

In the past decade, diamond has received much attention as a promising material due to its unique combination of desirable electrical, optical, and mechanical properties [Wer 98]. Unfortunately, it has proved very difficult to exploit these properties, due to both cost and scarcity of large natural diamonds, and the fact that diamonds are only available in the form of small stones. With much hard work and research chemical vapor deposition techniques were developed to grow thin diamond films on non-diamond substrates [Cla 91].

Thin film technologies continue to evolve and their use is broadening. If the hype is to be believed, thin films will advance every industry using them. With applications as widespread as data storage, automotive alloys, optical coatings, medical devices, medicines and electrical components, thin films coatings are the next technology to watch. Recent figures suggest the market was worth $ 24 billion in 2001 and will grow to $ 81 billion by 2008. Diamond films can be used for all the applications mentioned above, it may become as the 21st century material [May 00] [Cla 91] [Pre 97].

Diamond and hard carbon coatings are widely used to improve the micro tribological properties of micro electro mechanical systems (MEMS) [Wan 02] [Wer 01]. Due to its hardness, wear resistance as well as robustness to harsh environment diamond is an attractive material for many MEMS applications, e.g. micro grippers and atomic force microscope (AFM) probes. These micro components could be fabricated by selective deposition of polycrystalline diamond or hard carbon films on silicon substrates and molds, using silicon dioxide (SiO_2) as a sacrificial layer [Shi 00] [Ban 04a] [Ban 05].

Recently, diamond films have been gaining attention because of their piezoresistive nature, which makes them an attractive material for MEMS transducers. Single crystalline as well as polycrystalline diamond shows piezoresistive behavior [Wer 98] [Yam 05] [Asl 92]. Higher the value of the piezoresistive gauge factor (K) higher is the sensitivity of the transducer. Boron-doped polycrystalline diamond exhibits a considerable piezoresistive effect with gauge factors of a few hundreds and more than 4000 under inter- and intra-grain probing conditions, respectively [Sah 98]. In a recent study a best value of the piezoresistive gauge factor of 50 was reported for boron-doped polycrystalline diamond on oxidized silicon substrates [Yam 04]. Gauge factor depends on the resistivity of the polycrystalline diamond where gauge factor increases with the resistivity. Maximum values of 70 - 80 were obtained at around 10^{-2} Ωcm [Tan 05] [Wer 98].

Furthermore, crystalline diamond films are bio-compatible and along with their piezoresistive nature are very attractive for sensors in the medical field [Tan 05].

However, diamond films have certain limitations: (1) they require high temperature ($\geq 700\ ^0$C) for their growth, thereby limiting the choice of the substrate for e.g. it is not favourable for the deposition on micro-structured silicon, (2) it is difficult to achieve smooth surface morphology for polycrystalline diamond, (3) it is not easy to deposit them uniformly on large surfaces and (4) it is difficult to grow large crystalline diamond at reasonable growth rates [Des 89].

This necessitates the need for another type of film, which retains most of the properties of diamond and can overcome the above mentioned limitations to a large extent. These films are amorphous in nature and are called “diamond-like carbon films”. They were invented by Aisenberg and Chabot in 1971 by quenching a beam of C+ ions accelerated in a vacuum of 2 mPa to a negatively biased substrate [Ais 71]. The attractive properties of this material have led to a large amount of research on the deposition, characterization and on the development of relevant applications. Diamond-like carbon (DLC) is a generic term for thin hard carbon films, which can be prepared by numerous techniques including rf-sputtering, rf plasma-assisted chemical vapor deposition (PACVD), pulse laser deposition and ion beam methods [Sil 03]. Properties of DLC range from being highly conductive to highly insulating, hard to rather soft, and opaque to almost transparent. The reason for this great diversity is the structural and composition variation. Carbon exists in sp^3, sp^2 and sp^1 hybridization. The sp^3/sp^2 ratio of DLC matrix depends on the growth techniques and conditions, hydrogen concentration, gases used and doping of the films [Rob 94]. In this work we will concentrate on amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H) films.

Other low-temperature deposition such as plasma-enhanced or -assisted CVD, of hydrogenated amorphous (a-Si:H) and microcrystalline (µc-Si:H) silicon at low substrate temperature (< 150 °C) has received much attention [Ces 03] [Alp 02]. An investigation of the piezoresistive properties of low-temperature µc-Si:H on plastic substrates revealed gauge factors in the range of 10 - 40 [Alp 02]. Not enough investigations have been done to study the piezoresistive effect of the DLC films so far.

DLC is superior to heteroepitaxial and polycrystalline diamond in terms of production cost and process requirements in the sense that high substrate temperatures and additional doping sources are not necessary. Compared to a-Si:H and µc-Si:H it provides better tribological properties and resistance to harsh environment.

DLC films can be deposited on large surfaces and on almost any substrate with high deposition rate, depending on the deposition method used and parameters such as gases, bias voltage and pressure used during deposition.

DLC films are already very popular for their mechanical and optical properties [Myu 03] [Smi 84] [Tam 89] [Jia 89]. Various commercial products are available that take advantage of its tribological and optical properties. Because of their hardness, low friction coefficient in humid conditions [Ban 04] [Ban 04 a] [Enk 80] they are ideally suited for many high-demand wear applications that cannot be handled by ‘traditional’ coatings. DLC films are used for ultra thin overcoats on hard disks [Liu 98], Video cassette recorder (VCR) head drums (where DLC coatings have lowered the friction coefficient by 14 to 30 % and reduced wear rate by 50 % [Lee 95]), protecting coatings for magnetic tape heads and polycarbonates [Dam 02]. Because of its tribological properties in combination with optical transparency in the infrared and visible range, tuneable optical bandgap and refractive index, it is used as surface protection coatings in infrared (IR) optics [Bub 83] [Let 87] and antireflection coating in solar cells [Aro 04] [Let 87] [Mor 82]. DLC films are also gaining popularity in bio-medical field because of their bio-compatibility with blood and cells [Yan 04] [Let 87]. Biological sensors of the future will need to operate at the interface of biology and modern microelectronics. Since the DLC films can be deposited on Si and structured, bio-sensors can be developed using them.

This work deals with the development of a smart washer using DLC films -given the films have piezoresistive behaviour [Lüt 05].

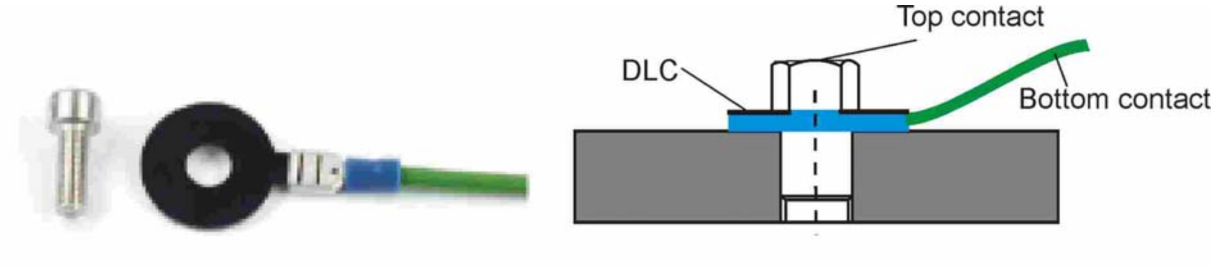

Figure 1 Schematic of smart washer coated with DLC in a screw joint [Lüt 05].

The schematic of smart washer coated with DLC in a screw joint is shown in Figure 1. One side of the washer is covered with the DLC film (Figure 1). The screw is the top contact and the washer itself the bottom contact. The screw is tightened on the washer, which exerts force on the DLC film. If the DLC films have piezoresistive behaviour, the change in resistance due to the applied force can be measured; telling the screw it has tightened firmly when a certain amount of resistance is reached or giving an alarm when the screw has worked itself loose. Using similar principle one can develop a smart gripper, smart vice and other smart mechanical parts.

The above discussed applications have been major motivation for this work. The other motivation was to integrate DLC films with silicon in order to use it as a MEMS device for harsh environments, and to develop force/pressure sensors from it.

This contribution examines the structural and electrical transport properties of sputtered a-C and plasma-assisted chemical vapour deposited (PACVD) a-C:H as a material for piezoresistive strain gauges in MEMS. The current transport mechanism in the films at both room temperature and at higher temperatures is studied. The heterojunction of DLC/Si is studied so that devices can be manufactured using it. In this study the piezoresistive properties of a-C and a-C:H strain gauges integrated on a bulk micromachined silicon are addressed for the first time. An extensive study was undertaken to measure the gauge factor of a-C and a-C:H films at different temperatures, voltages and under longitudinal, transversal, tensile and compressive strain configurations. The gauge factor was measured by changing the deposition parameters of the a-C:H films. Finally a model was introduced to explain the origin of piezoresistance in the a-C and a-C:H films and parameters which can further enhance the value of gauge factor in the films.

1 Preparation techniques for diamond-like carbon

Thin film technologies continue to evolve and their use is broadening. In fact, with the growing need for component and assembly miniaturization, well established thick film processes are rapidly approaching their technological limits. As a result, more and more manufacturers of electronic, mechanical, chemical, optical and energy supply devices now are considering replacing conventional thick film processes with thin film technologies to manufacture smaller components and parts. In addition, thin film technology allows the creation of new families of products; modifying and enhancing the properties of bulk material by deposition on top a thin layer having different composition and morphology.

Due to their desirable electrical, optical, and mechanical properties diamond films have gained a lot of attention [Wer 98] [May 00] [Cha 04], but it has certain disadvantages (discussed in introduction), which are hugely overcome by DLC films resulting in DLC films getting popular. However, before the films can be used in devices their properties have to be known which is not the case at the time being. In order to reduce this knowledge gap, characterization of current transport mechanism and structural properties of DLC films is performed in this work.

DLC films are introduced briefly in this chapter, followed by description of deposition methods of a-C and a-C:H films, which were used in this work.

1.1 Diamond-like Carbon films

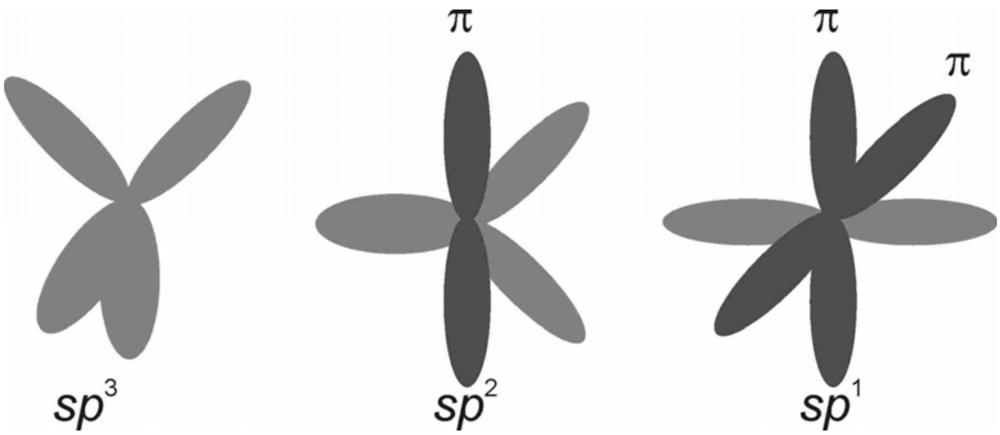

Figure 1.1 The sp^3, sp^2, sp^1 hybridized bonding [Sil 03].

Carbon is one of the most fascinating elements, because it gives rise to many different bonding configurations sp^1, sp^2 and sp^3 (Figure 1.1). It can form the stable trigonally (π) bonded crystal structure graphite, which is soft, optically opaque, electrically conducting and chemically active. Carbon can also form the metastable tetragonal bonded (σ) crystal structure diamond, which is the hardest material ever discovered, transparent from far ultraviolet to the far infrared, insulating and chemically inactive. Carbon, with the dilution of hydrogen, can also form polymer like structures.

In the sp^3 configuration, as in diamond, a carbon atom's four valence electrons are each assigned to a tetrahedrally directed sp^3 orbital, which makes a strong σ bond to an adjacent atom. In the three-fold coordinated sp^2 configuration as in graphite, three of the four valence electrons form strong σ bonds in a plane and the fourth one lies in π orbital, which lies normal to the σ bonding plane. This π orbital forms a weaker π bond with a π orbital on one or more neighboring atoms resulting in the layered structure of graphite. In sp^1 configuration, two of the four valence electrons enter σ bonds and the other two enters π bonds [Sil 03] forming the string like structures of polymers.

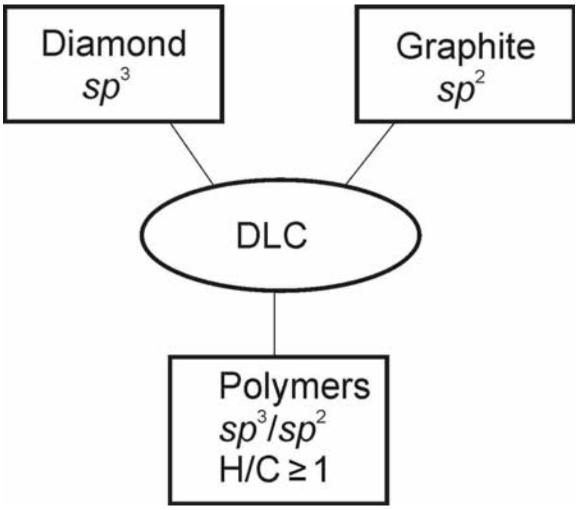

Figure 1.2 Limitations of DLC properties by the properties of diamond, graphite and hydrocarbon polymers [Cla 91].

By controlling the amount of graphite, diamond and polymer phase a new type of material can be formed broadly classified as diamond-like carbon [Cla 91] (Figure 1.2). If the so developed film is hard in nature it is termed as DLC, i.e. the more the percentage of sp^3 bonds the more the film is diamond-like. In general to produce diamond a very high temperature is needed, but DLC films can be grown on a variety of substrates over large areas, even at room temperature. This opens up new areas of interest for the scientists and technologists to use it for a variety of different applications.

1.2 Nomenclature

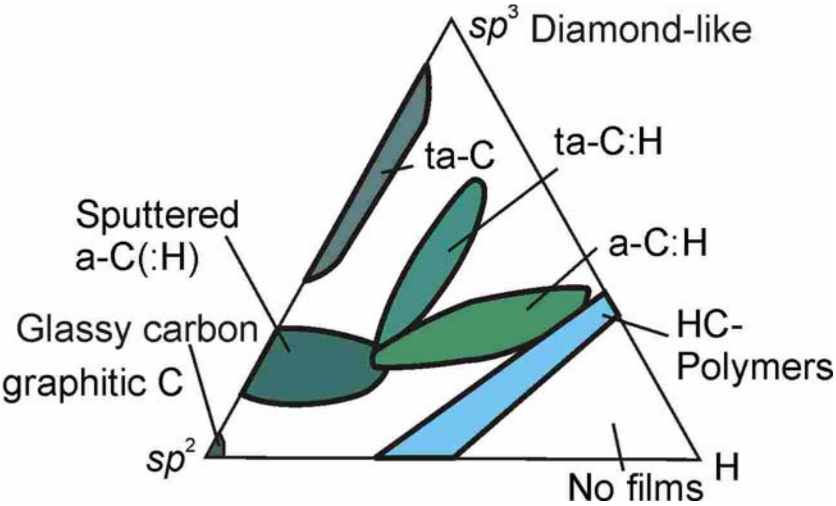

Figure 1.3 Ternary phase diagram of bonding in amorphous carbon-hydrogen alloys [Rob 02].

Diamond-like carbon was coined in 1971 by Aisenberg and Chabot [Ais 71] for ion-beam deposited amorphous carbon thin films that showed properties resembling diamond as opposed to graphite. These films were found to have mixed phases of diamond and graphite but no long range order i.e. they were amorphous in nature.

So the term "*diamond-like*" emphasizes a set of properties akin to diamond and at the same time implies the absence of crystalline diamond order. By this definition, *all diamond-like carbon films are amorphous, but not all amorphous carbon is diamond-like*.

DLC films consist of a mixture of sp^2 and sp^3 bonding which depends on the growth techniques and conditions, hydrogen concentration and doping on the films etc. A variety of nomenclature comes into the picture depending upon the preparation techniques and properties (Figure 1.3).

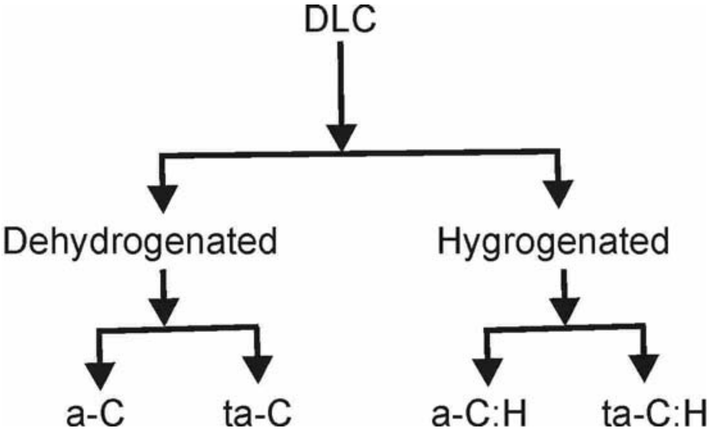

Figure 1.4 Classification of diamond-like carbon films.

Amorphous carbon (a-C) containing mostly graphite phase is prepared by pyrolysis, thermal evaporation and are very soft as compared to DLC. The various forms of DLC may be broadly classified into two categories, hydrogenated (right part of Figure 1.4) and dehydrogenated (left part of the Figure 1.4). The hydrogen free films can be further divided into amorphous carbon (a-C) and tetrahedral amorphous carbon (ta-C), where a-C has less percentage of sp^3 bonds compared to ta-C. The films with hydrogen can also be further divided into hydrogenated amorphous carbon (a-C:H) and tetrahedral hydrogenated amorphous carbon (ta-C:H), where a-C:H has less percentage of sp^3 bonds compared to ta-C:H. Tetrahedral films are more diamond-like compared to a-C and a-C:H.

Typical properties of the various forms of DLC are compared to diamond and graphite in Table 1.1.

Table 1.1 Basic properties of several crystalline and amorphous carbon materials [Rob 02] [Cla 91].

Material	Density (g/cm^3)	Bandgap (eV)	Hardness (GPa)	*sp*^{3} (%)	H (%)
Graphite	2.27	0	-	-	0
Glassy carbon	1.3 - 1.6	0	2 - 3	~ 0	~ 0
Evaporated C	1.9 - 2.0	0.4 - 0.7	2 - 5	< 5	< 5
Sputtered a-C	2.2 - 2.6	0.6 - 0.9	10	5 - 10	< 5
ta-C	2.9 - 3.4	2.5	100	> 85	< 5
Hard a-C:H	1.6 - 2.0	1.2 - 1.6	10 - 30	40 - 50	30 - 50
Soft a-C:H	0.9 - 1.2	1.6 - 4	< 5	50 - 80	50 - 60
Polyethylene	0.9	6	0.01	100	66
Diamond	3.52	5.5	100	100	0
Si	2.33	1.12	13	-	-
GaAs	5.31	1.43	6.8	-	-
SiC	3.2	3.03 - 3.26	25	-	-
GaN	6.1	3.45	10.8	-	-