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ELECTRICAL AND OPTICAL PROPERTIES OF "DIAMONDLIKE" CARBON FILMS

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ELECTRICAL AND OPTICAL PROPERTIES OF "DIAMONDLIKE" CARBON FILMS

by

A. Azim Khan

A DISSERTATION

Presented to the Faculty of

The Graduate College in the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Interdepartmental Area of Engineering (Electrical)

Under the Supervision of Professor John A. Woollam

Lincoln, Nebraska

August, 1983

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TITLE

ELECTRICAL AND OPTICAL

PROPERTIES OF "DIAMONDLIKE CARBON FILMS

BY

Abdul Azim Khan

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ELECTRICAL AND OPTICAL PROPERTIES OF "DIAMONDLIKE" CARBON FILMS

Abdul Azim Khan, Ph.D

University of Nebraska, 1983

Adviser: John A. Woollam

ABSTRACT--Hard, insulating, amorphous-carbon films have been deposited on single crystal silicon substrates using ion beam sputtering, rf glow discharge in methane and dc sputtering of a graphite target in an Ar ambient. Electrical and optical properties of these films have been studied.

The interfacial electrical properties have been evaluated using MIS capacitance and conductance measurements both as a function of gate voltage with frequency being a parameter, and as a function of frequency with gate voltage being a parameter.

For ion beam sputtered films, equivalent parallel conductance data showed a good fit to theory only if either a single time constant or else a continuum of states is assumed. Commonly observed anomalous dispersion of time constants was not noted in these samples.

For MIS samples made with dc sputtered amorphous-carbon film, the data indicated a tunnelling type of mechanism for the observed ac loss. Measurements for these samples were taken both under dark and various lighting conditions in the frequency range of 100 Hz to 10 MHz. For both (ion beam and dc sputtered) types of samples, density of interface

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states has been evaluated and found to be fairly low from a device point of view.

Optical constants of ion beam sputtered and rf glow discharge deposited films have been determined using multiple wavelength, multiple angle of incidence measurement technique of null ellipsometry. All measurements were four zone and the wavelength range was 253.6 nm to 632.8 nm. Both as-prepared and annealed samples were used. It was found that the refractive index and the extinction coefficient show only a minimal systematic change as the samples are annealed upto 500 °C.

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NOMENCLATURE

Symbol	Definition
C_c	Measured capacitance corrected for the ohmic losses
C_i	Capacitance of the insulating layer
C_{id}	Total capacitance of the ideal MIS structure
C_{it}	Capacitance due to the interface traps
C_m	Measured capacitance of the MIS structure
C_{min}	Minimum value of the high frequency capacitance
C_p	Equivalent parallel capacitance
C_s	Silicon surface capacitance (depletion capacitance)
σ_n	Electron capture cross section of an interface trap
σ_p	Hole capture cross section of an interface trap
D_{et}	Volume density of the empty insulator traps
D_{it}	Interface state density
d	Insulator traps distribution distance
d_{it}	Surface density of the interface traps
E_c	Electronic energy at the conduction band edge
E_f	Electronic energy at the Fermi level
E_{fm}	Metal Fermi level
E_g	Semiconductor band gap
E_i	Electronic energy at the intrinsic Fermi level
E_o	Kinetic energy of an electron
E_t	Energy position of an insulator trap
E_v	Electronic energy at the valence band edge
E_{op}	Optical band gap

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NOMENCLATURE

Symbol	Definition
e_n	Electron emission constant
f_o	Fermi function established by V_{GO}
$f(t)$	Fermi function at time t
G_c	Measured conductance corrected for the ohmic losses
G_m	Measured conductance of the MIS structure
$G_n(t)$	Electron emission rate
G_p	Equivalent parallel conductance
$g(x,E_t)$	Pseudo Fermi function in the variable x
h	Planck's constant
$Im(Y_{it})$	Imaginary part of the complex admittance
$J_s(t)$	Surface current density through interface states
K	Volume density of insulator traps
K_i	Dielectric constant of the insulator
K_s	Dielectric constant of the semiconductor
$K_t(x,E_t)$	Distribution function of the insulator traps
k	Boltzmann's constant
k_o	Electron wave function decay constant (wave vector)
L_D	Intrinsic Debye length in the semiconductor
N_A	Acceptor concentration
N_D	Donor concentration
N_t	Number of electrons trapped in the insulator per cm^2 per second
N_{ft}	Total number of filled insulator traps

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NOMENCLATURE

Symbol	Definition
n_i	Intrinsic carrier concentration
n_s	Electron concentration at the surface
$n_s(t)$	Electron concentration at the surface at time t
n_{so}	Surface concentration of electrons established by V_{GO}
P	Probability of an electron capture by an insulator trap
p_s	Hole concentration at the surface
Q_G	Charge on the metal field plate
Q_h	Charge due to holes at the surface
Q_{it}	Charge in the insulator traps
Q_s	Net total charge at the semiconductor surface
Q_{ss}	Charge in the interface states at zero bias
$Q_{ss}(t)$	Charge in the interface states at time t
q	Magnitude of the electronic charge
$Re(Y_{it})$	Real part of the complex admittance
$R_n(t)$	Rate of electron capture by the interface states
R_s, R_b	Interface state and bulk resistances respectively
R_p	Insulator leakage resistance
T	Absolute temperature
τ	Electron delay time within the forbidden region
t_i	Thickness of the insulating layer
u	Dimensioless potential (i.e., potential in units of kT/q)
u_f	Dimensioless Fermi potential
u_s	Dimensionless surface potential

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NOMENCLATURE

Symbol	Definition
u_{so}	Dimensionless surface potential established by V_{Go}
V_{fb}	Flat band voltage shift
V_G	Voltage applied to the gate (gate bias)
V_{Go}	A particular value of the gate bias
V_i	Potential drop across the insulator
V_{it}	Potential drop at the insulator traps
v_{th}	Thermal velocity of the electrons
x_d	The effective width of the depletion region
$x_d\|_{max}$	Maximum width of the depletion region
x_{inv}	The effective width of the inversion layer
x_m	Maximum trap occupation distance during the measurement
Y_{it}	Complex admittance of the MIS structure
α	Optical absorption coefficient
β	Dimensionless parameter; $\beta = 2K_od$
γ	Decay constant of the exponential trap distribution
Δ	Phase angle of the complex reflectance ratio; an ellipsometric parameter
ϵ_o	Permitivity of free space
η	Refractive index
k	Extinction coefficient
λ	Wavelength
ν	Frequency
σ	Standard deviation of the statistical model

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NOMENCLATURE

Symbol	Definition
σ_n	Electron capture cross section of an insulator trap
$\sigma_n(x)$	Effective electron capture cross section for an insulator trap located at x
τ	Time constant of a single level interface state. Also denotes time constant of an insulator trap located at the interface
$\tau(x)$	Time constant of an insulator trap located at x
τ_m	Mean time constant of a continuum of interface states located within $\sim kT/q$
τ_n	Electron life time
τ_p	Hole life time
ϕ_f	Fermi potential
ϕ_M	Metal work function
ϕ_{MS}	Metal-semiconductor work function difference
ϕ_s	Silicon surface potential
χ_s	Semiconductor electron affinity
ψ	Amplitude of the complex reflectance ratio; an ellipsometric parameter
$\psi(x)$	Electron wave function
ω	Angular frequency

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CHAPTER I

INTRODUCTORY REMARKS

"Diamond-like" amorphous-carbon films are readily distinguishable from other forms of carbon films because of their many unusual properties. These properties include (but are not restricted to):

1. Optical transparency -- more or less depending upon the methods of preparation. Low infra-red (IR) absorption.
2. High electrical resistivity -- ranging from 10^6 - $10^{12}\Omega$-cm.
3. Very good adhesion to diverse substrates. These include, insulators (plastics), semiconductors (Si, Ge), metals (Al, Cu),etc.
4. Unusually smooth surface, in some cases films are smoother than the substrate.
5. Excellent resistance to corrosive chemicals -- including HF, HNO_3, acetone, methanol, trichloroethane, etc.
6. Extreme hardness -- can scratch glass.
7. High index of refraction -- about 2 in the visible range.
8. High dielectric constant -- between 8-16 depending on the method of preparation.
9. High dielectric breakdown voltage -- 10^6 V/cm.
10. Diamond-like structure -- quasi-amorphous films show crystallites in the 50 - 100 Å range. It has been claimed that these crystallites have a cubic lattice with lattice constants that are close to those for cubic diamond (1).

Carbon films with many of these properties were first produced by

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Aisenberg and Chabot using an ion beam technique (2). Since then attempts have been made to deposit such films using a number of other techniques, such as, cracking of hydrocarbons in a glow discharge (3-5), ion beam sputtering from a carbon target (6), etc. Amorphous-carbon films produced by these various techniques are in general smooth, hard and semi-transparent and exhibit a wide range of physico-chemical properties. That is, they often have varying ranges of values for the ten properties listed above. Most of the available literature therefore deals with the investigation of various deposition techniques and the physico-chemical properties of the resulting deposits.

The unique properties of a-carbon films make them potentially ideal for a number of applications in electronic devices, in optical components, and as environmental protection coatings. However, as discussed in chapter VI, there is a wide range of reported optical properties for this material. The situation in regard to electrical and interfacial electronic properties is even worse. Resistivity is the only electrical property that has been measured for most samples. Again, the reported values span several orders of magnitude in what is purported to be the the same material.

The research program at the University of Nebraska aims at a thorough characterization of high resistivity a-carbon films. The research described in this dissertation is part of that program. The dissertation is divided into VI Chapters. Chapter I is a brief introduction. Chapter II establishes the fundamentals of the theory of admittance measurements and describes the various interface state models currently in vogue. Chapter III is a detailed description of the various experimental setups used in this research. Chapter IV describes the results of admittance

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measurements on ion beam sputtered samples. The admittance spectroscopy research on ion beam sputtered samples was of preliminary character; hence, the results arrived at in this Chapter--although complete--are not based on extensive measurements. Chapter V describes the main thrust of this work. It discusses the interfacial electronic properties of Al/a-C/p-Si MIS structures in considerable detail. The amorphous-carbon films were made by sputtering of a graphite target in an Ar ambient. Chapter VI addresses another important objective of this work: an understanding of the optical properties of high resistivity amorphous-carbon films. In this chapter, the results of detailed ellipsometric measurements on as-prepared and annealed amorphous-carbon films are presented and discussed.

For the sake of simplicity, all equations, diagrams and tables are numbered separately for each chapter. All notation is explained in the notation section in alphabetical order. An appendix provided at the end discusses the data acquisition and analysis computer programs in considerable detail. The programs have been written in Fortran IV with all attempts made to make them machine independent. These programs should therefore be easily adaptable to any mini-computer with a Fortran compiler. Copies of the programs are available from the author upon request.

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CHAPTER II

THEORY OF ADMITTANCE MEASUREMENTS

2.1 INTRODUCTION

Perhaps the most important building block of many modern integrated circuits is the so-called MIS (metal-insulator-semiconductor) transistor. Also known as IGFET (insulated-gate field effect transistor), this device is also in wide use as a discrete component. In silicon-based technology, where the insulator is a thermally grown native oxide, one usually speaks of MOSFETs (metal-oxide-semiconductor field effect transistor). The cross section of a basic MOSFET is shown in Fig. 2.1 for the case of an n-channel device formed on a p-type substrate, which is usually lightly doped with acceptor impurities while the n^+ source and drain contacts are formed by diffusing or implanting a large concentration of donor impurities. The metal (usually aluminum) gate is separated from the Si bulk by a thin (several hundred Å) layer of oxide. When a sufficiently high positive voltage is applied to the gate, enough positive charges are accumulated on the gate metal to create a thin (.50 Å) image sheet of mobile electrons at the insulator-semiconductor interface. This is the "channel" of the FET and the gate voltage modulates the conductance of this channel. Appropriate voltages are imposed on the source and the drain contacts for proper operation of the device.

Although the basic aim of all IGFET research is to create devices using different dielectrics and/or semiconductors that will operate using an inverted layer of mobile charge as outlined above, the achieve-

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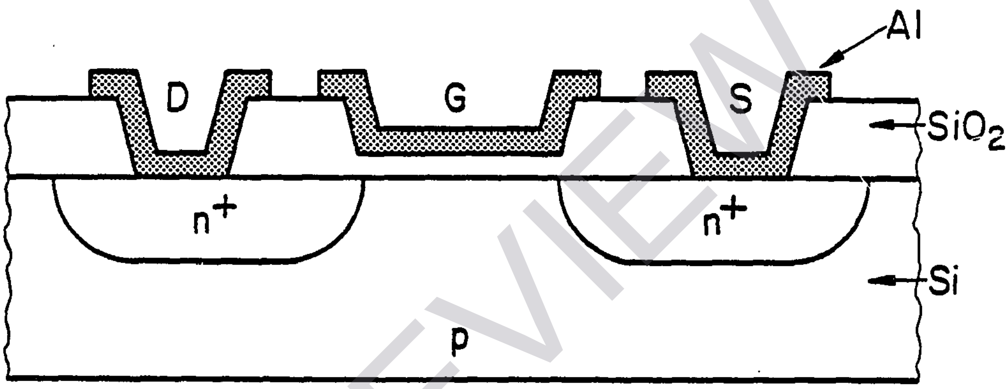

FIG. 2.1 Cross section of a typical silicon based MOSFET

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