SCHOTTKY DIODE FABRICATION

USING ULTRAVIOLET

PHOTON-ENHANCED CHEMICAL VAPOR DEPOSITION

Philippe Cuaz B.A. Physics, Reed College, 1986

A thesis submitted to the faculty of Oregon Graduate Center in partial fulfillment of the requirements for the degree Master of Science in Electrical Engineering

May, 1989

The thesis "Schottky Diode Fabrication Using Ultraviolet Photon-Enhanced Chemical Vapor Deposition" by Philippe Cuaz has been examined and approved by the following Examination Committee:

> Rajendra Solanki, Thesis Research Advisor Associate Professor Department of Applied Physics and Electrical Engineering Oregon Graduate Center

> John S. Blakerhore Professor Department of Applied Physics and Electrical Engineering Oregon Graduate Center

Jean F. Delord	
Department of	Physics
Reed College	

ACKNOWLEDGMENTS

I am indebted to my advisor, Dr. Raj Solanki whose concrete guidance and support helped me see this thesis to completion. I would also like to thank Dr. John S. Blackemore whose class was determinant in my understanding of Schottky Diodes. I am grateful to Nyles Cody, U. Sudarsan, and Bill Tang for numerous useful suggestions.

I am also thankful to Dr. Jean F. Delord for his participation on my thesis examination committee and his careful examination of this thesis.

Finally, I am most indebted to my mother for her continual encouragement, and to my grandfather for his financial assistance.

Table of Contents

.

ACKNOWLEDGEMENTSiii		
LIST OF FIGURES AND TABLESvi		
ABSTRACT		
1. INTRODUCTION		
1.1 Historical Development		
1.2 Short Introduction to Schottky Barrier		
Diode Theory5		
1.3 Applications14		
2. FABRICATION TECHNIQUES		
2.1 Evaporated Contacts		
2.2 Sputtered Contacts		
2.3 Chemical Vapor Deposition25		
2.3.1 Nucleation of Thin Film for		
Chemical Vapor Deposition27		
2.3.2 Thermal Dissociation of Metal		
Carbonyl Compounds		
2.3.3 Tungsten Hexafluoride Reduction32		
2.3.4 Silicon Reduction of Tungsten		
Hexafluoride		

	2.3.5 Hydrogen Reduction of Tungsten
	Hexafluoride
	2.3.6 UV Assisted Chemical Vapor
	Deposition
	2.3.7 Molecular Photodissociation
3.	. EXPERIMENTAL SETUP
	3.1 The UV Source
	3.2 The Reactor
	3.3 The Gas Control System
	3.4 The Pressure Controller, Valve, and Vacuum
	Pump
	3.5 The Procedure
4.	. RESULTS AND DISCUSSION
	4.1 Arrhenius Plot of Mo(CO) ₆ 51
	4.2 I-V Characteristics of Schottky diodes54
5.	CONCLUSION
R	EFERENCES63

v

List of Figures and Tables

1 Formation of a Barrier Between a Metal and		
Semiconductor		
2 Built-in Potential of Abrupt Junction as a Function		
of Impurity Concentration		
3 Avalanche Breakdown Voltage Versus Impurity		
Concentration for Abrupt Junctions9		
4 Transport Process in a Forward-Biased Schottky		
Barrier		
5 The Structure of a Bipolar n-p-n Transistor with		
a SBD Clamp		
6 A Schottky-Barrier Gate FET17		
7 Dissociation		
Table 1 Carbonyl Partial Pressure		
8 Photodissociation		
9 System Configuration		
10 The Procedure		
11 Arrhenius Plot for Mo(CO) ₆		
12 I-V Characteristics for Schottky Diodes		
13 Log I-V Characteristics for Two Mo/n-GaAs		
Schottky Diodes		
Table 2 Compilation of Process Parameters and		
Electrical Characteristics		

ABSTRACT

SCHOTTKY DIODE FABRICATION

USING ULTRAVIOLET

PHOTON-ENHANCED CHEMICAL VAPOR DEPOSITION

Philippe Cuaz

Oregon Graduate Center, 1989

Supervising Professor: Dr. Raj Solanki

The purpose of this work was to determine the feasibility of using a UV enhanced chemical vapor deposition (UVCVD) process for fabrication of Schottky diodes of refractory metals on GaAs. The UVCVD process allows low temperature deposition which is important for processing III-V compounds.

Precursor gases were metalorganic carbonyls and halides of the refractory metals. Substrates included GaAs and Si. The deposition parameters were first optimized and activation energy calculated.

In the second part of the work, electrical properties of Schottky diodes were examined. The current versus voltage characteristics are considered for determining the barrier height of the diodes which can then be compared to theoretical values and other reported measured value.

Both chemical and electrical results can be used to improve the process at hand, UV

vii

enhanced chemical vapor deposition, by determining which process parameters should be changed.

INTRODUCTION

To realize the importance of a metal-semiconductor contact one must see its present use and foresee its potential future. At the present time, through the inherent need to connect the different building blocks of an integrated circuit¹, metal-semiconductor connection is essential. Such connection is commonly referred to as *ohmic contact* when the relationship between voltage and current is linear and *rectifying* when this relation is non-linear. The general trend for future applications of semiconductor contacts will reside mainly in improved materials involved in interconnections, and in new processing techniques enhancing their topological characteristic and allowing new design implementation of circuits and solid state devices.

In the present study, the discussion will be centered on film deposition using photodeposition, characterisation, and comparison to theoretical values of rectifying contacts. While ohmic contacts, inherent to their quasi-complementary nature (if it is not ohmic, it is rectifying), can not be ignored, they will only be referred to improve the understanding of the theory supporting the physical phenomena involved. This experimental work was conducted on doped gallium arsenide substrates using a UV enhanced chemical vapor deposition process. Rectifying metal-semiconductor contacts are called Schottky Barrier Diodes (SBD) or just Schottky diodes. Their non-linear

behavior, that is a sudden and very large increase in current for a small change in voltage (forward bias) attracted the attention of researchers a long time ago.

HISTORICAL DEVELOPMENT

Historically, it was Braun, in 1874, who first reported metal-semiconductor rectification. Since then, rectifiers have experienced three major periods of industrial importance: as radio detector at the beginning of the century, as radar detector during WW2, and recently as clamping diode in integrated circuit.

Radio detectors were made of point contact diode or "cat's whisker". That is a sharpened metal wire directly in contact with a semiconductor surface. The area of such junction is very small and of hemispherical shape. The contact was made by pressure or alloying. The reliability of this technique is very poor and its reproducibility is very low. The advent of DeForest's triode vacuum tube in the 1920's supplanted point contact for radio detection. It was then mainly used for measuring u.h.f. power until the development of microwave radar during WW2.

For microwave radars, point contact diodes offered much lower noise operation as frequency converter and low level microwave detector than the high frequency vacuum tube detector of that period. Their intensive development was to contribute to the invention of the point contact germanium transistor in 1948-9 by Bardeen and Brattain. As pn junction transistors became available in the 1950's, the role of metal semiconductor contact was reduced mainly to ohmic contact for junction devices.

In about 1960, the invention of the planar process (and the Field Effect Transistor) led to a better understanding of interface and surface cleaning techniques wich became essential in the making of reliable and reproducible (planar) Schottky diode.

From then on, durable commercial applications started to appear.

SHORT INTRODUCTION TO SCHOTTKY BARRIER DIODE THEORY

To see how a Schottky barrier may form when a metal comes into contact with a semiconductor, suppose that the metal and the semiconductor are both electrically neutral and separated from each other. The energy band diagram is shown (in fig. 1) for an n-type semiconductor with a work function less than that of the metal; this is the most important case in practice, and we suppose that there are no surface states present. If the metal and semiconductor are connected electrically by a wire, electrons pass from the semiconductor into the metal and the two Fermi levels are forced into coincidence as shown(b). The energy of electrons at rest outside the surfaces of the two solids are no longer the same, and there is an electric field in the gap directed from right to left. There must be a negative charge on the surface of the metal balanced by a positive charge in the semiconductor. The charge on the surface of the metal consists simply of extra conduction electrons. Since the semiconductor is n-type, the positive charge will be provided by conduction electrons receding from the surface, leaving uncompensated positive donor ions in a region depleted of electrons. Because the donor concentration is many orders of magnitude less than the concentration of electrons in the metal, the unconpensated donors occcupy a layer of appreciable thickness w, comparable to the width of the depletion region in a p-n junction, and the bands in the semiconductor are bent upwards as shown. The difference V_i between the electrostatic potentials outside the surfaces of the metal and the semiconductor is given by $V_i = \partial E_i$ where ∂ is their separation and E_i the field in the gap. If the metal and semiconductor approach each other, Vi must tend to zero if Ei is to



19. 1: Formation of a barrier between a metal and semiconductor
(a) neutral and isolated,
(b) electrically connected,
(c) separated by a narrow gap,
(d) in perfect contact.

O denotes electron in the conduction band; + denotes donor ion.

PHIm: metal work function PHIs : semiconductor work function PHIb : barrier height

Xs : electron affinity of the semiconductor

Ec : energy of bottom of conduction band in semiconductor

Ef : Fermi energy

Ev : energy of top of valence band

remain finite and, when they finally touch , the barrier due to the vacuum disappears altogether and we are left with an ideal metal-semiconductor contact(d). It is clear from the fact that as V_i tends to zero that the height of the barrier PHI_b measured relative to the Fermi level is given by:

(1)
$$PHI_b = PHI_m - X_s.$$

In most practical metal semiconductor contacts, the ideal situation shown (d) is never reached because there is usually a thin insulating layer of oxide, about 10-20 Å thick, on the surface of the semiconductor(c). Such an insulating film is often referred to as an interfacial layer. A practical contact is therefore more like that shown(c); however, the barrier presented to electrons by the oxide layer is usually so narrow that electrons can tunnel through it quite easily, and is almost indistinguishable as far as the conduction electrons are concerned.

Another way to obtain the ideal barrier height uses a more empirical approach. First, we must define a few terms. Let V_n be the potential difference between the Fermi level and E_c (the bottom of the conduction band). Knowing that PHI_b is the barrier height, we can define the built-in potential V_{bi} as:

(2)

Therefore

$$PHI_b = V_{bi} + V_n$$

The value of V_n can be deduced from the impurity concentration :

(4)
$$V_n = (KT/q) * ln(N_c/N_D)$$

where	K : Boltzman constant;	T: absolute temperature;
	q : elementary charge;	N _D : donor density;

N_c: effective density of states in conduction band.

Also, the value of V_{bi} can be obtained from the existing curve (Fig. 2) of built-in potential of abrupt junction in GaAs as a function of impurity concentration.



Fig. 2: Built-in potentials of abrupt junctions as

a function of impurity concentration.31

A good way to evaluate the impurity concentration is to use the breakdown voltage of the IV characteristics of the Schottky diode(Fig.3):



Fig. 3: Avalanche breakdown voltage versus impurity concentration for abrupt junctions.⁹

This way is much more empirical than the simplistic barrier height evaluation from the difference between metal work function and semiconductor electron affinity.

It is believed that a better accuracy can be achieved by including Fermi level pinning at the surface. The model preferred (only referred here to state the possible inacuracy encountered in the use of work function) is called the effective-work-function(EWF) model¹⁸, in which the Fermi energy position at the surface (or interface) is not due to or fixed by surface states but rather related to the work function of the microclusters of the one or more interface phases resulting from contamination prior to reactions which occur during metallization. This yields the following relation:

(5)
$$PHI_b = PHI_{eff} - X_s$$

where PHI_{eff} is an appropriately weighted average of the work functions of the different interface phases.

For most of the III-V compounds, including GaAs, conventional metallization, i.e., non-UHV conditions, results in a condition in which PHI_{eff} is due mainly to PHI_{v} , to work function of the group-V component, and occurs as a result of the following reaction:¹⁸

(6) V-O + III-V --> V + III-O

where V-O and III-O are generic group-V and -III oxides.

The next theoretical point of importance is the current transport mechanism involved in a Schottky diode. The various ways in which electrons can be transported across a metal-semiconductor junction under forward bias are shown schematically for an n-type semiconductor (Fig. 4). The inverse processes occur under reverse bias. The mechanisms are:⁹

 (a) emission of electrons from the semiconductor over the top of the barrier into the metal;

(b) quantum-mechanical tunnelling through the barrier;

(c) recombination in the space-charge region;

(d) recombination in the neutral region ('hole injection').

We are only interested in the most important one for our purpose, and this is emission



Fig. 4: Transport processes in a forward-biased Schottky barrier

over the barrier.

The current voltage relationship predicted by the thermionic-emission theory is of the form of the ideal rectifier characteristic⁹

(7) $J = J_S * \{ exp(qV/kT) - 1 \}$

with

(8)
$$J_s = A'' T^2 \exp(-q PHI_b / kT),$$

where A" : effective Richardson Constant(110 and 8 amp/K² for

n-type Si and GaAs respectively);

- k : Boltzman constant;
- q : elementary charge;
- T : absolute temperature;

provided the barrier height is independent of the bias, which we shall assume in our case, thus ignoring barrier height lowering from image-force effects.

Now, to evaluate the transport mechanism in a Schottky diode, it is useful to refer to the ideality factor n. From the theory⁹ of generation-recombination current in a diode, n tends to 1 when diffusion current dominates, and it tends to 2 when recombination current dominates. Its value depends on the empirical forward current formula:

(9)
$$J = J_{s} \exp[qV / nkT] \text{ for } V >> kT/q$$

where ${\rm J}_{\rm S}$ is the saturation current, therefore the ideality factor n is defined as: 9

(10)
$$\mathbf{n} = (\mathbf{q}/\mathbf{kT})^* \partial \mathbf{V} / \partial (\ln \mathbf{J}).$$

The purpose of this section was to introduce some theoretical background on which one can reasonably evaluate the quality of the processed diodes. These concepts will be utilized when discussing the properties of the Schottky diodes fabricated. The next section will introduce the basic motivations for processing Schottky diodes as applications are concerned.

APPLICATIONS

Application to integrated circuit^{1,2} started with the patent of Baird³ in 1964 for Schottky barrier clamp integrated to silicon bipolar transistor. In 1966, an FET with a Schottky barrier gate or metal-semiconductor field effect transistor (MESFET) was described by Mead. Other developments during this period appeared: planar Schottky varactor and varistor for microwave application. Since then few new applications have been made. Some IR detectors and solar cells use the Schottky effect but the most promising future is still in saturation preventing clamps in high speed bipolar integrated circuit and high frequency diode and transistor for signal detection and amplification in microwave communication systems.

Integrated Circuit Applications:

Bipolar technology:4,5,6

By forward biasing a Schottky diode between the base and the collector of an npn bipolar transistor, one can achieve considerable reduction in the storage time T_s.

In the saturation region, the collector junction of the transistor is slightly forward biased. Now, if the forward voltage drop in the diode is much lower than the base collector ON voltage of the transistor, most of the excess current flows through the SB diode where minority carriers are not stored (it is a unipolar, majority carrier device).

It has been shown that the measured tso , saturation time constant, of the composite



Fig. 5 : The structure of a bipolar n-p-n transistor with a SBD clamp.⁵





transistor is shorter by 10 to 50% from that of the original transistor while the voltage margin against the circuit fluctuation was reduced by half (from 0.6v to 0.3v) which is a tradeoff for speed but it will not be a fatal disadvantage. This circuit may easily be integrated on a monolithic silicon wafer because of its simple structure.

Mesfet technology:7,8

By laying down a metal gate over a diffusion area, a metal semiconductor contact is obtained. Using these processing steps, it is easy to convert a Mesfet into a Schottky diode. Placing ohmic contacts on the source and the drain and then connecting them together with a metal strip, one gets two diodes in parallel, with input at the gate. Such a diode is widely used in GaAs digital integrated circuits for level shifting the voltage between different stage of a design. A good example is the Schottky diode FET logic (SDFL) which uses both Mesfets and Schottky diodes to perform logic functions and has been proposed as an alternative to BFL(Buffered FET Logic) in LSI circuit implementation. Very attractive speed-power trade-offs have been obtained with SDFL. Multilevel logic can be achieved using this logic approach.

Mosfet technology:

Swapping the contacts type for a Mosfet device, that is using Schottky-barrier diodes at the source and at the drain, and an ohmic contact at the gate, improves the performance of the FET by minimizing the short channel effects and the source series







resistance. Also, eliminating high-temperature annealing steps can promote better quality in the oxides and better control of geometry. This structure can be made on semiconductors where a pn junction cannot be easily formed.

Metal-Semiconductor Photodetector:9,10,11

Schottky barrier diode can be used as high efficiency photodetector. To avoid absorption losses and large reflection when the diode is illuminated through the metal contact, the metal film must be very thin (about 100A) and an antireflection coating must be used. Metal-Semiconductor photodiodes are particularly useful in the visible and ultraviolet regions but also in the IR. In the UV and visible regions, the absorption coefficients (a) for most of the common semiconductors are very high, of the order of 10^5 cm⁻¹ or more, corresponding to an effective absorption length of 1/a =0.1um or less. It is possible to choose a proper metal and a proper antireflection coating so that a large fraction of the incident radiation will be absorbed near the surface of the semiconductor.

Solar Cells:9,12,13

Schottky barrier solar cells must have a thin enough metal film to allow a substantial amount of the light to reach the semiconductor. There are three photocurrent components. Short-wavelength light entering the semiconductor is mainly absorbed in the depletion region. Long-wavelength light is absorbed in the neutral region, creating electron-hole pairs. The electrons must diffuse to the depletion edge to be collected. For

solar cell application the excitation of carriers from the metal into the semiconductor can be neglected. Schottky barrier solar cells have advantages including low temperature processing because no high temperature diffusion is required, adaptability to polycrystalline and thin film solar cells, high radiation resistance due to high electrical field near the surface, and high current output and good spectral response. The solar cell efficiency increases with its barrier height. The maximum efficiency is about 25% which is comparable to homojunction efficiency.

Varistor:9,14

A varistor (variable resistor) is a two terminal device that shows nonhomic behavior. It is used as symmetrical fractional voltage(0.5V) limiter by connecting two diode in parallel oppositely poled. The two diode unit will exhibit the forward IV characteristics in either direction.

Varactor:9,15,16

The term "varactor" comes from the words variable reactor and means a device whose reactance can be varied in a controlled manner with a bias voltage. Varactor diodes are widely used in parametric amplification. harmonic generation, mixing, detection, and voltage variable tuning.

Rectifier:9,17

A rectifier is a diode that is specially designed to rectify alternating current, that is, to pass current only in the forward direction and therefore it can be used as an a.c. to d.c. converter. A single device usually suppresses or attenuates alternate half-cycles of the alternating-current input.

In the following chapters, the discussion will first focus on the different processes that can be used to fabricate Schottky diodes, and particularly on chemical vapor deposition and UV enhanced chemical vapor deposition which were used in this work. Then, the attention will be centered on the actual setup and procedure involved in the fabrication. Finally, the last chapter will attempt to analyse and evaluate both the process at hand and the resulting diodes.

CHAPTER TWO

FABRICATION TECHNIQUES

The most important metallization techniques for discrete devices and integrated circuits are physical vapor deposition and chemical vapor deposition. Physical vapor deposition is done under vacuum using either an evaporation or sputtering technique. Chemical vapor deposition is done either at atmospheric pressure or at low pressure and can be energy-enhanced.

Evaporated Contacts:

The overwhelming majority of practical contacts are made by either evaporation or sputtering. Most evaporated contacts are made in a conventional vacuum system pumped by a diffusion pump giving a vacuum around 10⁻⁵ Torr, usually with a liquid-nitrogen trap. The lower-melting-point metals such as aluminium and gold can usually be evaporated quite simply by resistive heating from a boat or a filament, while the refractory metals like molybdenum, titanium, and tungsten are generally evaporated by chemical etching, and this invariably produces a thin oxide layer of thickness about 10-20Å; the precise nature and thickness depend on the exact method of preparing the surface. The effect of surface preparation on the characteristics of evaporated Schottky

barriers on silicon has been discussed by Turner and Rhoderick(1968). Interfacial layer can also be caused by water or other vapor adsorbed onto the surface of the semiconductor before insertion into the vacuum system. Such adsorbed layers can usually be removed by heating the substrate to between 100C and 200C prior to evaporation(Smith,1969).

Even if the semiconductor surface were devoid of an oxide layer to start with, as would be the case if it were prepared by cleaving a crystal so as to expose a fresh surface, an oxide layer would form by exposure to air in the time taken to transfer the semiconductor to a vacuum chamber and pump the system down to its final pressure. For example, in a vacuum of 10⁻⁵ Torr the gas molecules which strike the surface would, if they all adhered, built up a monolayer in about 10^{-1} s³⁷. If the sticking coefficient is as low as 10⁻³, as it is believed to be for oxygen on silicon ³⁸, it would take much longer (100s) for a monolayer to build-up. However, the semiconductor surface is exposed to much higher presures for several tens of minutes during the pump-down period, so there is plenty of time for an oxide to form. The pump-down period can be avoided if the surface is prepared by cleavage or ion etching within the vacuum system after the final pressure has been reached, but an oxide layer can still be formed during the evaporation unless the vacuum is maintained at 10⁻⁷ Torr or better while the evaporation is in progress. To maintain pressure of this order requires a good vacuum system, because the heat produced during the evaporation accelerate outgassing. An interfacial layer may also form as a result of the adsorption of vapour from a diffusion pump, and Cowley³⁹ has shown that this source of contamination can be avoided by the use of an ion pump. For this reason it is now common to use ion-pumped systems capable of achieving a vacuum of 10⁻⁷-10⁻⁸

Torr.

The only way of ensuring that there is no interfacial layer is to evaporate a film onto a semiconductor immediately after it has been cleaved in an ultra-high vacuum at a pressure around 10^{-10} Torr^{40,41,42}. The time taken for a monolayer of adsorbed gas atoms to form at this pressure is so long (10^7 s) that there is virtually no possibility of interfacial layer being established or of the metal film being contaminated. But although contacts prepared in this way may be chemically ideal, they are still not physically ideal because of the mechanical damage to the surface during the cleaving process, and they frequently show current/voltage characteristics with ideality factors n considerably greater than unity. This method of preparing contacts is far too slow and cumbersome to be used in industrial processes, and there is no potential advantage in doing so.

Sputtered Contacts:

Sputtering is frequently used to make contacts to practical devices because it produces metal films with good mechanical adhesion. It is beginning to supplant evaporation in semiconductor technology because it gives better control of deposition rate and disintegration. The object to be coated is placed near the cathode of a gas discharge tube, the cathode being made from the desired metal to be deposited. The whole system is formed as a demountable assembly that is evacuated to the correct pressure to form a gas tube. Typical operating conditions are at pressures between 1.0 and 0.01 Torr and anode voltages between one and 20 kilovolts. It is very important in industry even though it has

poor energy efficiency(5-10% compared with 35% for e-beam).

We can distinguish several kind of sputtering processes. Triode sputtering and magnetron sputtering are used when high electron density is required in the discharge to avoid surface oxidation as for the sputtering of AI. These kinds of sputtering both use magnetic fields to capture the electrons and increase their ionizing efficiency. Ion beam sputtering is also used for metal and insulator. It uses variable ion current and energy with lower pressure chamber than in conventional sputter process. This implies lower "contamination" from the surrounding inert gas and higher growth rate. But this setup is not yet designed for batch processing .

Chemical Vapor Deposition (CVD):

Simplicity and efficiency of chemical vapor deposition makes it an attractive process for industrial applications. Simplicity to achieve batch processing and efficiency to obtain good resistivity and good step coverage are among the most important factors at stake. Chemical vapor deposition is actually the decomposition of a gas composed of at least two different species(elements, radical, etc.). By breaking the bonds linking the species, one obtains decomposition. From the nature of the species involved different reactions may occur. The decomposition may occur either on the surface of the substrate where the gas is adsorbed or before adsorbtion, that is when the gas is introduced in the reactor and did not yet react with the surface. In the last case, the species decomposed have "dangling" bonds which are prone to link themselve together to form cluster of atoms

before condensing on the surface. In the first case, decomposition is achieved by desorption on the surface after adsorption. Thus, the growth rate will depend on both the type of decomposition reaction and the surface reaction. Generally, these reactions are driven pyrolytically (heat energy) or/and by reduction:

 WF_6 + thermal energy --> W + $3F_2$ WF_6 + $3H_2$ --> W + 6HF

WCI6 + 3H2 --> W + 6HCI

The nature of the bonds linking the different species will determine the amount of energy to be provided to achieve decomposition. To attain the desired decomposition temperature, different kind of systems can be used. In a "hot wall" system the reactor tube is surrounded by a furnace. A "cold wall" system uses rf induction heating to reach the target temperature while the walls of the reactor are water cooled. Evaluation of these systems are based on substrate contamination and gas efficiency.

While pyrolysis is often used, alternative energy forms are possible for decomposition. In particular, plasma or optical energy (from UV lamp or laser) can drive the decomposition reaction instead of heat only:

WF₆ + plasma or optical energy --> W + 3F₂

The film growth will depend eventually on the mechanism of nucleation at the surface. Nucleation of Thin Films for Chemical Vapor Deposition:

The nucleation of atoms from the gas phase onto the substrate surface is critical for

Fig. 7: DISSOCIATION



DISSOCIATION IN THE GAS PHASE

thin film formation. Assuming an atomically clean surface, nucleation sites are formed if adsorption of gas phase atoms is greater than desorption at the surface. As an atom approaches a surface, it experiences a potential field arising from van der Waals and polarization forces. The interaction is weak, and as the atom enters a shallow potential well, it is physisorbed. Once physisorbed, the atom may react chemically, with the surface, in a process known as chemisorption. This is characterized by a chemical interaction between the gas and the surface as the atoms enter a deeper potential well with increased binding energy. The energy lost by the adatom as it enters this potential well is usually greater than 10 kcal/mole or 0.42 eV and, in an ideal case, the heat of adsorption, E_a , is proportional to the heat of formation of the chemical compound.

Adsorption can be quantified by a factor, $alpha_s$, defined as the sticking coefficient. The sticking coefficient is the ratio between the amount of film material condensed on the substrate to the amount that impinged the substrate. The coefficient is dependent on pressure, gas species, surface temperature and coverage of the surface with nucleation sites. For most gas-solid combinations we get: $0.1 < alpha_s < 1$. At constant temperature, adsorption has been shown to increase with increasing gas pressure, since adsorption increase with an increase in the concentration of atoms impinging on the surface.

Desorption of atoms from the surface is achieved with sufficient energy input. For physisorbed atoms, the amount of energy is usually equal to the potential well, while for chemisorption, the amount of desorption energy is generally greater than the adsorption energy. If the amount of desorption energy at the surface is consistently greater than the

adsorption energy, the film will be removed, rather than deposited. This process, known as ablation, is a mean of removing film and is not desirable for film growth. Ablation is primarily a problem for substrates with poor thermal conductivity. Silicon dioxide has a poor thermal conductivity compared to silicon, and therefore, ablation is more likely to occur on the oxide. The reflectivity of a surface can limit the amount of photon energy absorbed and thus, ablation can be reduced for highly reflective metal films. Since metals generally have high thermal conductivity and optical reflectivity, ablation will not be a serious problem when depositing metals by surface photon bombardment.

Thermal Dissociation of Metal Carbonyl Compounds:

A variety of organometallic compounds exist, including molybdenum hexacarbonyl, $Mo(CO)_6$; tungsten hexacarbonyl, $W(CO)_6$; and chromium hexacarbonyl, $Cr(CO)_6$. These organometallic carbonyl compounds, $M(CO)_X$, have a metal atom bonded to carbon monoxide molecules by the sharing of p orbital electrons. With sufficient energy input to the molecule, the bonds, also known as ligands, can be broken to free the metal atom. Most carbonyls experience initial dissociation of a CO molecule at temperature of 100-150°C. Only at temperature of 450°C does molybdenum carbonyl dissociate completely to release a metal atom. At this temperature, molybdenum thin films have been deposited by chemical vapor deposition with resistivities of about twice the bulk resistivity of 5.6 W/cm.
Carbonyl compounds generally have low vapor pressures at room temperature and are easily vaporized by moderate heat. The vaporized compounds may be transported to the reaction chamber by flowing a carrier gas through a reservoir containing the carbonyl. A list of the calculated partial pressures of various carbonyl compounds as a function of temperature is shown in table 1³⁶. As a result of carbonyl partial pressure, the carbonyl vapor will enter the reaction chamber even in the absence of a carrier gas flow and deposition will occur.

The deposition of metal films from the decomposition of carbonyl compounds is limited primarily by two rate controlling mechanisms. The reaction rate or kinetic limit is determined by the decomposition rate of the carbonyl, while the mass transport, or diffusion limit is characterized by the gaseous diffusion of the reactant species toward the substrate. In the reaction rate limit, thermal chemical decomposition of the carbonyl is described by the activation energy, E_a , which relates the deposition rate, Rd, to the temperature, by the relationship shown:

(11)
$$Rd = exp(-E_a/kT)$$

where k is Boltzmann's constant and T is the temperature in °K. The activation energy may be modified with additional energy input such as plasma or photon excitation.

In the case where the reaction rate is not a limiting factor, the deposition rate is controlled by the concentration of reactants in the reacton zone. In the low pressure regime, mass transport is controlled by the partial pressure of the reactants. Too low a reactant concentration results in starving the reaction. By increasing the partial

Tec	Partial Pressure (Torr)							
	Mo(CO)6	W(CD)6	Cr(CO)6					
30	0.27	0.06	0.28					
35	0.41	0.09	0.43					
40	0.63	0.14	0.68					
45	0.94	0.22	1.05					

Table 1: Carbonyl Partial Pressure

pressure to supply the reaction, the reaction rate limit can be achieved. On the other hand, atmospheric pressure reactions with sufficient reactant concentration are governed by the diffusion of the reactants through molecular boundary layers to replenish the reaction.

Tungsten Hexafluoride Reduction:

Tungsten Hexafluoride, WF₆, has emerged as one of the primary source gases for tungsten CVD. The tungsten hexafluoride molecule is an octahedral hexahalide with a $M^{6+}(d^{\circ})F_{6}^{-}$ electronic structure according to ligand field theory. The 5d⁴6s² electrons of tungsten are shared with the fluorine atoms and there is little orbital dependent metal-fluorine bonding. Dissociation of WF₆ is achieved through a ligand-metal charge transfer transition like carbonyl dissociation, where an electron from the ligand orbital transfers to the metal atom and reduces the attraction between the metal and fluorine atom. The process of removing the fluorine atoms bonded to tungsten hexafluoride, WF₆, to produce a metal atom is a reduction reaction. Reduction can be accomplished with silicon atoms or atomic hydrogen. For gallium arsenide, the reaction taking place is not well understood.

Silicon Reduction of Tungsten Hexafluoride:

The silicon reduction of tungsten hexafluoride has been explored considerably. Due

to the selective nature of tungsten deposition by this reaction, the tungsten can be deposited on polysilicon gates and diffused regions in MOS devices to act as current shunts for the metal interconnections. Other applications include contact metallization and diffusion barriers for aluminum to silicon contacts.

The silicon reduction of tungsten hexafluoride results in the depositon of tungsten atoms only on silicon surfaces. The reduction occurs very quickly and is expressed by the following reaction:

 $2WF_6(g) + 3Si(s) \rightarrow 2W(s) + 3SiF_4(g)$

where silicon is consumed in the reaction producing SiF₄.

The tungsten film is deposited until the reactants cannot diffuse through the deposited layer to react with the underlying silicon. This limitation occurs when the tungsten films achieve a thickness of 100-200 Å. The final thickness of the tungsten film depends mainly on surface silicon dioxide characteristics, and substrate temperature. The amount of silicon consumed by the reduction is approximately half the film thickness according to the following equation:¹⁹

(12) t_W formed/ t_{Si} consumed = $2M_W f_{Si}/3M_{Si} f_W = 0.525$

where t = thickness formed/consumed in the reaction = M/f M = molecular weight of the element, f = density. Hydrogen Reduction of Tungsten Hexafluoride:

In order to achieve metal films thick enough for first and second level interconnections in integrated circuits, hydrogen reduction of tungsten hexafluoride must be employed. The hydrogen reduction has been characterized in a variety of publications^{20,21,22,23}. This reduction produces a tungsten atom and hydrofluoric acid(HF), shown in the following equation:

$$WF_{6}(g) + 3H_{2}(g) -> W(s) + 6HF(g)$$

The thermal reduction mechanism of adsobed molecules is based on the Langmuir-Hinshelwood model²¹ consisting of the following steps, assuming a layer of tungsten is already present:

- adsorption of WF6 on the tungsten surface

- adsorption of H2 on the surface

- dissociation of H2 on the surface

- chemical reaction between WF_6 and H_2 in the adsorbed phase

- desorption of HF.

For the reaction rate limited process, the thermal activation energy of hydrogen reduction was calculated to be 0.71 eV²⁰. The reaction rate limit was reached when the concentration of WF₆ in the reaction chamber was sufficient to saturate the deposition

rate. However, in the mass flow control region, variation of the WF₆ concentration still resulted in changes in the deposition rate ²⁴. In the reaction rate limit, however, the deposition rate is dependent on the square root of the hydrogen partial pressure in the chamber and not on the partial pressure of WF₆^{20,21}. The kinetic data for the reaction rate limit can be approximated by the deposition rate equation shown below:²²

(13)
$$Rd = \{ P(H_2)^{1/2} P(WF_6)^0 \} exp (-0.71 eV/kT) \}$$

where k is Boltzmann's constant and T is the substrate temperature in degree Kelvin. Furthermore, the calculated activation energy of 0.71 eV, for the thermal hydrogen reduction closely matches the activation energy for the surface diffusion of H_2 on tungsten²².

One factor that has affected the deposition rate is the wafer position with respect to the flow of the reactant gases²⁵. Normal incidence of the gases on the substrate has produced a faster deposition rate by a factor of two, to 1000Å/min, than gas flow parallel to the wafer. The increase in the deposition rate may be due to a higher adsorption rate of reactant gases by the substrate.

UV Assisted Chemical Vapor Deposition:

UV assisted chemical vapor deposition is a modified form of conventional chemical vapor deposition, and therefore, most of the issues discussed for CVD above, also hold for the photo-assisted reactions.

In order to reduce pyrolytic energy provided for decomposition, we need an alternate energy source. That can be achieved by using some form of optical energy which reduces the total amount of heat to be provided to the system, implying a lower substrate temperature or process temperature. This is an advantage over other processes because: -no blistering (of refractory metal deposition) from thermal/expansion coefficient

mismatch between metal and semiconductor.

-use of III-V semiconductor compounds with fairly low evaporation temperature

possible (avoid diffusion of As from the surface for GaAs).

-growth rate superior or comparable to other systems.

The photon-assisted chemical vapor deposition process is not fully understood due to the complexity of the mechanisms involved in photodissociation. Photons can induce a variety of reaction mechanisms. The first mechanism is photodissociation in the gas phase. If the molecule absorbs sufficient photon energy, the bonds linking the species will be broken. The second dissociation mechanism is the photodissociation of an adsorbed molecule. The reaction mechanism is identical to the gas phase dissociation, except desorption of the non-metallic species is necessary for film purity. The third mechanism is pyrolytic dissociation induced by both photon absorption and heating of the substrate. The heat transferred from the substrate to the adsorbed molecule must be sufficient for dissociation. The last mechanism presented is the electron transfer reaction. In this case, a photon absorbed by the surface creates a free electron that is captured by the molecule, resulting in bond breakage. Results indicate that several of these reactions are taking place simultaneously.

Fig. 8: PHOTODISSOCIATION



PHOTO-DISSOCIATION IN THE GAS PHASE

Molecular Photodissociation:

Molecular photodissociation is initiated by the absorption of a high energy photon by a molecular compound. A photon is absorbed if the photon wavelength corresponds to the absorption spectrum of the molecule. The UV photons are absorbed by the atomic electrons, and this energy is distributed within the molecule. With this additional energy, the molecule enters an excited state and can achieve stability by breaking one or more molecular bonds or by ionization. These molecular processes can have different reaction channels dictated by the amount of energy absorbed. The mechanism for the multiphoton process in a carbonyl compound can be explained in the following way. Initially, the molecule absorbs a photon and enters an excited state. During the excited state lifetime, dissociation can occur. Photon absorbtion continues until all bonds are broken. The end result of the process is a metal atom in the the excited or ionized state. If in gas phase, the metal atoms in this excited state can readily recombine with other metal atoms in the same state to form clusters and reach a lower stable state. Whereas in a conventional CVD reaction, all the energy required for the molecular dissociation was thermal energy, photo-CVD at least part of the molecular decomposition is achieved via photo-dissociation. Hence, photo-CVD can be operated at lower temperatures.

A distinction between the gas phase and the surface phase reaction mechanism is critical in order to understand the contribution of the UV photons to the reaction. Photon-induced pyrolytic surface reactions can contribute to the reaction rate. This contribution may be in the form of modifying the surface adsorption of the gas species or

by thermally inducing a surface dissociation of the adsorbed species. Surface properties change once film growth is initiated, which may affect interaction of the surface with the photons.

CHAPTER THREE

EXPERIMENTAL SETUP

The experimental set-up consisted of a CVD reactor with a modification to allow in UV radiation.

The UV Source:

The photon source used for these depositions was a medium-pressure mercury lamp manufactured by Fusion Semiconductor Systems. It can deliver deep ultraviolet light spectrum which is adjusted through variation in bulb fill, use of band-pass filters, or change in dielectric mirrors as necessary. The standard spectrum delivered by the lamp ranges from 200 to 250 nm and peaks at 230nm. The total power in this range was 100 mW. This can be used for maximum effectiveness in pattern transfer with material of corresponding spectral response characteristics such as polymethyl methacrylate(PMMA). Microwave radiation is used to energize a spherical quartz lamp bulb which has no electrodes and consequently overcomes many of the basic limitations of conventional mercury arc sources. The magnetron and other components are cooled by exhaust air (or nitrogen at 50 psi in our experiment) which is drawn through the louver behind the reflector cavity and through cooling air intake holes in the bottom of the case.





-

The three basic components of the lamp system are the power supply, the lamp or Illuminator, and the controller. The controller was not used in our experiment. The power supply houses all interlock electronics in addition to a high voltage DC and a low voltage AC supply for the magnetron. The Illuminator houses the magnetron, lamp bulb, reflector cavity, optical system and shutter(in our experiment, the optical system and shutter were discarded). During operation, the magnetron power tube produces microwave energy at 2450MHz which is channeled through the waveguide to the reflector cavity. The reflector cavity is a four inch diameter sphere with an interior optical coating and a fine wire mesh screen over a three inch diameter circular opening. The lamp bulb is located at the center of the cavity. The screen over the cavity opening keeps microwaves inside the cavity but allows the UV light to pass out. The lamp bulb is an 0.8 inch diameter quartz sphere, filled with mercury and an inert gas, mounted on quartz stem with a stainless steel holder. The microwaves focused on the lamp bulb heat the gas and mercury causing the formation of a plasma emitting deep UV radiation. The lamp bulb is cooled by four compressed air jets (actually 50psi compressed nitrogen for lower temperature cooling) located inside the reflector cavity. To assure uniform cooling, the lamp bulb is rotated on its axis at about 300 RPM. Also, a low powered UV ignitor bulb directs UV radiation at the lamp bulb at the same time as microwaves are applied for instant ignition of the lamp bulb. As full power is reached, the ignitor bulb turns off. If cooling is not properly applied, the bulb starts to melt and finally wears out when all mercury is released through a breach (generally, a small round hole) on the surface of the sphere. Replacement of the bulb is easily performed by pulling the stem holder from a quick-release coupling.

The Reactor:

The deposition system consists of a stainless steel cold-walled vacuum chamber. The pressure in the reactor can be as low as 0.6 millitorr, but generally was around 1mTorr depending on the total amount of incoming gases flowing into the chamber. The reactor was loaded from the top (since the size and implementation of the side door is inadequate to secure proper handling of the sample). The temperature of the substrate was evaluated by chromel/alumel thermocouples placed on the substrate support. The top opening had a circular window to allow the light to come in. This window was made of Suprasil quartz which allowed radiation into the reactor. Under the substrate support, external to the reactor were the heating elements. These elements were composed of two Sylvania EVR tungsten halogen lamps of 500Watts each at 120V.

Before each run, the reactor walls and the top opening were thoroughly cleaned with methanol, to reduce contamination of the surface to be exposed. The substrate support was cleaned with emery paper.

Also, after each run, the window was cleaned from deposited film that was formed inspite of a continuous helium window purge. This was achieved by immersing the window for a few seconds in a Tungsten etchant bath (this worked for both tungsten and moly deposition). The etching time was not prolonged needlessly to avoid deterioration of the window. The reactor intake was heated with a uniform temperature gradient. The lower temperature was at the carbonyl reservoir and the higher temperature was next to the reactor, to avoid unnecessary condensation/deposition on the walls of the reactor intake.

This was achieved with a heating element (heater tape) that was wrapped around the intake. The temperature achieved by the tape was about 60°C at the reactor side of the intake, and about 40°C at the reservoir side. Thus, before each run it was desirable to wait for the temperature to stabilize and the metallic elements to warm up.

The carbonyl reservoir was a metallic cylinder, inside which a set of separating walls forced the incoming gas to flow through a winding path. By filling this path with carbonyl powder and with moderate heating (30°C measured at the bottom of the reservoir by RTD thermocouple, and 40°C at the top), the incoming gas carried the carbonyl toward the reactor. The input and output of the reservoir were always closed when not in use. Since the carbonyl vapor pressure is high, it evaporates readily without any heating.

The Gases Control System:

Three mass flow controllers and close-coupled valves (#1258B) from MKS, were used in our experiment. Their rating was 500sccm for the helium window purge, 200 sccm for metal-hexafluoride when in use, and 1000 sccm for the helium carrier going through the carbonyl reservoir.

Three temperature controllers were used. Two of them were Omega model 48 controller, one of them was for the reactor temperature and the other for the bottom of the carbonyl reservoir. This model(48) will cycle on and off within a very narrow differential to maintain the set temperature. Instead of using a regular temperature sensitive wire(chromel-alumel), the temperature of the bottom of the reservoir was

measured using an RTD element to achieve higher accuracy in temperature setting. The last temperature controller was an Eurotherm model 919 and was used for controlling both side of the reactor intake element. The sensor was placed on the top of the carbonyl reservoir and a non-controlling digital thermometer was placed on the reactor side of the intake, thus a careful temperature control was obtained. All heating tape elements were connected to their respective controller through Variac transformers.

The Pressure Controller, Valve, and Vacuum Pump:

To control the pressure inside the reactor with continuous incoming gas, we used a pressure controller MKS 252, a pressure sensor baratron MKS 222B mounted next to the reactor output, a digital readout MKS PDR-D-1 to monitor the pressure reading from the baratron, and a throttling valve MKS 253 placed between the vacuum pump and the output of the reactor. The vacuum pump in use was a Leybold-Heraeus Trivac rotary vane pump, model D60A for ultimate partial pressure of 3*10⁻⁴ Torr.

THE PROCEDURE

In the elaboration of an optimal procedure, we faced two alternate possible sequences of steps. There are three basic steps in the making of a Schottky diode: semi-conductor cleaning, metal deposition, and contacts(that is any kind of connection from the device to the real world). To understand the alternative at hand, we must further present the three steps.

Semi-Conductor Cleaning:

The procedure used to clean GaAs was first to rinse the sample with methanol to dissolve organic contamination, then slowly dip the (nitrogen dried) sample, for a duration of 3 minutes in a chemical solution of H_2O , H_2O_2 , and H_2SO_4 [1:1:5], at room temperature(300K), and then dried again with nitrogen. Thus our cleaning procedure was mainly done by an etching solution. The temperature of the etching solution was an important factor in achieving Schottky characteristics in the latter steps of the process. In case of higher temperature than room temperature the sample's polished side was getting unpolished (fogged-out), suggesting an irregular oxidation-etching process. It has not been possible to determine experimentally the native or reacted (during cleaning) oxide layer thickness, but others have shown that thin oxide layer on the surface result in increased variation in Schottky barrier height²⁶ and change in the ideality factor. This indicates that the current transport mechanisms involved are very sensitive to the oxide layer

thickness and the higher the ideality factor, the less emission transport mechanism over the barrier is occuring which is the dominant transport mechanism for a good Schottky diode. Thus, it is not surprising in our opinion that the most critical step in the making of GaAs Schottky diode is the cleaning of the semiconductor surface and its clean maintenance until the metallization step occurs. Furthermore, beside surface oxidation, surface contamination can also prevent consistancy and reproducible characteristics among similar diodes. Such contamination implies surface states at the interface between semiconductor and metal. It has been shown that it is possible to evaluate the interface state energy distribution from Schottky I-V characteristics²⁷, using an iterative method. The inherent existence of three kinds of surface states for metal-GaAs interface has also been reported²⁸, independently of the metal or sample orientation. Also, the lack of any adequately clean environment totaly limits any consistant analysis and effectively increases the chance of contamination.

The cleaning procedure for Si samples was much simpler and much less care had to be taken. The etching solution was of HF and DI water[1:10] for three minutes.

Metallization:

Metallization was achieved by UV enhanced chemical vapor deposition and was treated in chapter II as a special entity.

Contacts:

The need for contacts to evaluate the current behavior of our device should not be taken for granted. How perfect a device one's process achieves is quite useless if no proof of performance exists, or a care for reality. In our case, it was decided from the setting of the probes and the electrically conducting surface on which the sample was to be tested that the only contact to be "added" was on the back side of the sample. Indeed, having the metallized side of the sample facing the metallized holding surface, a crude but sufficient ohmic contact was achieved between the two metallic surfaces. Thus, by adding an ohmic contact on the back side of the sample(the unpolished and unmetallized side) was sufficient to realize the full connection of our diode to the curve tracer via a pair of testing probes respectively in contact with the metallic holding surface, and the ohmic contact on the back side.

At this point we should note that the absence of an adequate dark environment could affect our measurements but only to a negligeable degree.

The ohmic contact was achieved by evaporation at 10⁻⁶ Torrs of three Au/Ge[88/12] pieces weighting 8 mg each about 6 cm away from the mask and sample holder. The mask was made with two holes of different sizes to actually make two dots on the back side of the sample, thus allowing a check on the ohmic characteristics of the contacts. Similarly for contacts on Si samples, we used silver pellets.

The resistivity of such contact decreases significantly after annealing. The annealing procedure was achieved by rapid thermal anneal(RTA) to a target temperature of

.



450°C for a duration of one minute. This temperature was chosen as a function of the eutectic temperature. In agreement with Mukherjee's results²⁹, blistering appeared on heating beyond 450°C and 400°C for Mo and W, respectively. This blistering is due to thermal expansion mismatch between GaAs and the metal, and thin film stress. Mukherjee reports that no outdiffusion of Ga or As has been observed in W or Mo. Therefore, both of them have an excellent stability to GaAs. The annealing time and ramp to target temperature are also critical factor in order to avoid blistering. It appeared that RTA to 400°C in one minute induces blistering of Mo but slow (2h) ramp in furnace with Ar atmosphere to 400°C did not show any blistering. As a result, annealing was further avoided as a too lenghty process for only a negligeable gain in performance.

At this point we should review the possible alternate ordering of the steps of the process. We presented in order: cleaning, metallization, and contacts. An other sequence was also considered: contacts, cleanning, and metallization. This sequence avoided deterioration of the metal film during the contact step: by doing the evaporation of the gold before metallization, the metalic film cannot be altered as it could during the handling of the sample on the holder and positioning of the mask, and this is an advantage. The disadvantage is for the cleaning step. First, only one side of the sample should be exposed by floating it on the etching solution. Then, it appeared that annealing prior to cleaning seems to induce more often the "fogging out" of the polished side than with the original sequence.

CHAPTER FOUR

RESULTS AND DISCUSSION

The evaluation of a process can be achieved by observing some results. Like a benchmark, one kind of result generally does not span over the full potential or limitation of such process but rather highlights only some special characteristics. To achieve a better coverage of the process at hand, UV enhanced chemical vapor deposition, we decided to look at two kinds of data. One is the growth rate versus temperature curves or Arrhenius plot whose slope actually can give some information on the chemistry of the process. That is how the chemical reaction involved in the process is happenning. This kind of data is very direct, allowing direct comparison with other processes but is it sufficient? We felt that the ultimate test could not be based on some direct data ignoring the functionality of the device to be made. Thus, the second other data were the IV curves of the Schottky diodes made. While IV characteristics give some good qualitative information on the electrical behavior of the diode it lacks the quantitative information found in the Log plot of the IV curve. Therefore, both types of curve were considered.

Arrhenius Plot of Mo(CO)6:

The log of growth rate versus inverse absolute temperature(1000/T) curve for $Mo(CO)_6$ on GaAs appears on Figure 11. It is possible to evaluate the activation energy E_a from the slope of the curve (see eq.11 p.31). It is the energy necessary to break the bound between Mo and $(CO)_6$ during vapor deposition. The lower the activation energy, the less heating is necessary, since most of it can be taken from the UV light. The energy provided by the photons is captured by the carbonyl molecules and thus the thermal energy required to break the bond between the metal M and the carbonyl (CO)6 is lowered by the amount of photon energy available. Therefore, a low activation energy means a low process temperature which reduces the chance of blistering of the metal from thermal expansion coefficient mismatch between semiconductor and metal. It was found:

at 5 Torr: Q=0.1323 eV (Mo: 25sccm, He: 800sccm)

and

at 2 Torr: Q=0.09291 eV (Mo: 25sccm, He: 800sccm)

These results seems to imply a slight dependence on pressure which is not well understood. The partial pressure (actual flow*total pressure/total flow) of Mo decreases at lower total pressure. It means, for the same volume, the number of molecule present is decreasing at lower total pressure, and thus, there are less M-(CO)6 bonds to break, therefore the amount of energy required to break these bonds must decrease. And this might be the reason the activation energy Ea is decreasing at lower total pressure.



Fig. 11: Arrhenius plot for Mo-(CO)6

1000/T

Now, we must compare these data to purely pyrolitic CVD processes. Such processes³⁰ give a value of 0.99 eV (1 eV = 23.053 kcal/mol). And, the higher the activation energy, the steeper is the slope of the Arrhenius curve. We therefore can say, the lower the activation energy is, the lower the processing temperature will be. And this is quite important to avoid blistering of refractory metal occuring at high temperature and to avoid outdiffusion of semiconductor species on the surface of the substrate (as for As in GaAs).

Now we must talk about our second set of data to conclude our process analysis.

I-V Characteristics of Schottky Diodes:

The goal of our investigation on the IV characteristics of Schottky diodes was to extract the ideality factor n from the log plot and use this ideality factor n to determine the current transport mechanism involved. Such transport will depend on both the potential barrier height and shape at the interface metal-semiconductor. And this barrier depends directly on the work function of both metal and semiconductor. Knowing the current transport mechanism, it is possible to strictly evaluate the quality of the Schottky diodes processed, and thus to determine the quality of the process not on chemical dissociation reaction grounds but on functionality achievement. And this functionality, by a reverse reasonning, can lead us back to steps of the process which might need to be improved or to be more understood as the chemistry of work function for example.

First, we want to present regular IV plots of three different kind of diodes that were investigated. The top diode of figure 12 is a Mo-GaAs Schottky diode which is similar to the three other Molybdenum diodes achieved. As easily observed, both the breakdown voltage and the forward voltage are far from ideal. Their shallow curvature suggests a definite problem with the conduction mechanism. More typically, a shallow breakdown can be induced by three phenomena grouped under the word "leakage current":

-Poor isolation on the side of the sample which let a surface current flowing from the metal film to the ohmic contact dot on the back side of the sample.



Fig. 12: I-V Characteristics for Schottky Diodes

-High impurity concentration or surface states due to contamination on the substrate which narrows the width of the barrier height and thus, allows easy tunneling of charge carrier through it and reduces emission transport mechanism as principal mechanism.

-Lowering of the barrier height.

The diode on the middle is a W-nGaAs Schottky diode, and its breakdown voltage is between 5 and 6 volt which gives an impurity concentration of about 5*10¹⁷cm⁻³. The lower the impurity concentration is, the more negative the breakdown voltage becomes. The IV characteristics of this diode are reasonably good, and the leakage current is almost nonexistant.

The last diode on Figure 12 is a W-Si Schottky diode and it has a breakdown voltage of at least 10 volt (actually between 15 and 20 volts, which gives an impurity concentration of about 5*10¹⁶cm⁻³). Some leakage current is noticeable after -4 volt. The fact that we have leakage current for both GaAs and Si Schottky diodes might suggest that the leakage current is not due to semiconductor specific preparation steps but to a common reason as surface contamination that both type of semiconductor share.

Now we want to use the log curve of two Mo-nGaAs Schottky diodes that have been processed at the same time (figure 13) to illustrate the analysis we did on all the diodes made. We observe a flattening of the curve at higher voltage. This is due to recombination current. We can clearly distinguish two sets of data. Each one





-

. .

. .

: •

corresponds to one diode, thus, process variations are important but do not occur during deposition, either before at cleanning time or after at contact time. The different graphical representations(cross, square, oval, ...) indicate that different pictures from the curve tracer had to be taken to cover the range of interest. The barrier height that can be expected can be calculated in the following way³¹ (as shown in Chapter I):

(3)
$$PHI_b = V_{bi} + kT/q^* ln(N_c/N_d)$$

 V_{bi} is about 0.70 eV from fig 2 page 8 since we found an impurity concentration N_d of 4.5*10¹⁷ cm⁻³. N_c is about 4.7*10¹⁷ cm⁻³ for GaAs at 300K. Thus, Vn = 0.001 eV and $PHI_b=0.70 \text{ eV}$. From the log of the IV curve, the saturation current J_s can be evaluated, and from eq. (8) page 12, the barrier height becomes:

 $PHI_{b}=kT/q \ *In(A^{*}T^{2}/J_{s}),$

where A* is 8 and 110 for n-GaAs and n-Si respectively.

=0.64 eV for the top curve, and

=0.67 eV for the bottom curve.

To have a final answer on the quality of these two processed diodes, we want to find their ideality factor. In chapter I, we have shown the ideality factor can be extracted from the following relation:

(10) $1/n = kT/q * d(\ln J)/dV.$

For the evaluation of the slope we care only about the steepest and straightest part of the curve :

For the top curve we found: n=3.31

For the bottom curve: n=4.13

A similar analysis can be used for Si Schottky diode. V_{bi} is 0.4 eV since we found an impurity concentration of 5*10¹⁶ cm⁻³. Nc is

2.8*10¹⁹cm⁻³ at 300K which gives a value of 0.163 eV for Vn. Therefore the expected barrier height is PHI=0.56 eV.

To see the different results we obtained for both Si and GaAs we tabulated our results (table 2). This table shows both the diode-process in use with its parameters and the electrical characteristics extracted from the log of the IV curve of these diodes. The barrier height obtained are higher than expected for Si and lower than expected for GaAs. Mo/n-GaAs diodes have a reported measured barrier height of about 0.9 eV^{32,33,34}.

The difference PHIm-Xs predicts: 4.6-4.07=0.53 eV, where 4.6V is the value of the work function for polycrystalline Mo after Michaelson(1977)⁴⁴, and 4.07V is the value for the electron affinity of GaAs⁹. Similarly, W/n-GaAs diodes have a reported measured barrier height of about 0.71 eV³⁵, and PHIm-Xs predicts 4.55-4.07=0.48 eV. Finally, W/Si diodes have a reported measured barrier height of about 0.67 eV³⁵, and the predicted barrier height is 4.55-4.05=0.5eV. Thus, there are wide variations between prediction for barrier height from PHIm-Xs, Vbi+Vn, reported measured values, and our own results. The average value of the barrier height for the fabricated W/Si diodes is 0.69 eV which is much higher than expected values Vbi+Vn=0.56 eV and PHIm-Xs=0.5 eV but only 0.02 eV higher than the reported measured value of 0.67 eV. Similarly, the

run #	metal	s/c	type	°C	Pr. T.	time min	rate Å/min	W He ccm	H2 ccm	₩ ccm	Mo ccm	Js µA	Area cm2	Phi eV	n
21	WF6	51	th	275	2	60	14.09	70	450	200		10	0.3	0.68	2.45
22	WF6	Si	th.	347	2	60	71.95	70	650	200		12	.412	0.68	3.86
27	WF6	51	UV	300	2	20	14.40	70	850	200		4.3	1.33	0.74	2.46
33	WF6	GaAs	UV	250	2.1	30		150	850	200		5.6	1.08	0.66	10.5
57	MoCO6	GaAs	UV	150	5	30	169.0	800			25	50	0.45	0.58	11.2
66	MoCD6	GeAs	UV	150	5	22	183.9	800			25	5	0.4	0.64	3.31
66	MoCO6	GeAs	UV	150	5	22	183.9	800			25	1.4	412	0.67	4 13
67	MoCD6	GaAs	UV	100	5	30	121.5	800			25	320	0.33	0.52	7.0
79	WC06	GeAs	UV	150	0.8	20		200		30		48	585	0.59	11.7
BO	WCD6	GaAs	UV	150	0.8	30		400		30		300	.39	0.53	5.7
81	WCD6	GaAs	UV	150	1	30		600		30		200	.525	0.55	1.94

Table 2: Compilation of Process Parameters and electrical characteristics

.

average value of the barrier height for the fabricated W/n-GaAs diodes is 0.58 eV which is much lower than the expected value Vbi+Vn=0.70 eV and the reported measured value of 0.71 eV but much higher (0.1 eV) than the predicted value PHIm-Xs=0.48 eV. Finally, the average value of the barrier height for the fabricated Mo/n-GaAs diodes is 0.60 eV which is much lower than the expected value from Vbi+Vn=0.70 eV and the reported measured value of 0.90 eV but higher than the predicted value from PHIm-Xs=0.53 eV.

The ideality factor are generally much higher than one, which implies a poor functionality. This means the processed diodes are not good diodes. It is difficult at this stage and from the diversity of results to determine the transport mechanism precisely. Tunneling might be the major transport mechanism in the Si diodes since they have high barrier heights. The low barrier heights in GaAs diodes actually do not favor tunneling, thus it might suggest an emission transport mechanism over the barrier. Moreover, the wide variation of the results can not reveal any dependence between the process parameters and the electrical characteristics achieved.

CONCLUSION

While, the Arrhenius plot shows quite clearly that the UV enhanced deposition mechanism has a lower activation energy, the electrical characteristics fail to reveal dependence from process parameters. Nevertheless, this attempt was not useless, and it shows that the process still has to be improved. For that matter, one should reconsider each step of the process. Cleaning should be improved in several ways. First, control of open-air contamination should be achieved, then the width of the oxide layer grown during etching should be carefully monitored. Deposition should be improved by realizing complete dissociation of carbonyl molecules. The non-dissociated molecules, M(CO)_X for x<6, are embeded in the film and might contribute to surface contamination. Achieving a low-pressure CVD might improve the purity of the metallic film. Finally, contacts should be also improved to give low resistivity. The variation in result might be partly due from the poor control of surface contamination. It is only when this basic problem can be resolved that correlation between electrical characteristics and process parameters will show up.

REFERENCES

- J.M. Andrews, <u>The role of the metal-semiconductor interface in silicon</u> <u>integrated circuit technology</u>, J. Vac. Sci. Technol., Vol. 11, No. 6, Nov./Dec. 1974, p.972.
- V.L. Rideout, <u>A Review of the Theory. Technology and applications of</u> <u>Metal-Semiconductor Rectifiers</u>, Thin Solid Films, 48 (1978), pp. 261-291.
- 3) U.S. Patent 3,463,975 (August 26, 1969), to J.R. Biard.
- Kunio Tada, Jose Luis R. Laraya, and Bunkyo-ku, <u>Reduction of the Storage Time</u> of a Transistor Using a Schottky-Barrier Diode, Proceedings of the IEEE, November1967, p. 2064.
- Yasuo Tarui, Yutaka Hayashi, Hiro Teshima, and Toshihiro Sekigawa, <u>Transistor</u> <u>Schottky-Barrier-Diode Integrated Logic Circuit</u>, Journal of Solid-State Circuits, Vol. SC-4, No. 1, February 1969, p. 3.
- R.H. Baker, <u>Maximum Efficiency Transistor Switching</u> <u>Circuits</u>, Technical Report No. 110, M.I.T., Lincoln Lab., 22 March 1956.

- H. Ishikawa, H. Kusakawa, K. Suyama, and M. Fukuta, <u>Normally-off GaAs</u> <u>MESFET for low power, high speed logic circuits</u>, IEEE Int. Solid-State Circuits Conf. Tech. Digest, February (1977), pp. 200-201.
- H. Morkoc, J. Andrews, R. Sankaran, and J.H. Dully, <u>Tungsten/Gold Gate GaAs</u> <u>Microwave F.E.T.</u>, Electronics letters, 3rd August 1978, Vol. 14, No. 16, p. 514.
- 9) S.M. Sze, <u>Physics of Semiconductor Devices</u>, 1981.
- Bor-Yeu Tsaur, Melanie M. Weeks, and Paul W. Pellegrini, <u>Pt-Ir Silicide</u> <u>Schottky-Barrier IR Detectors</u>, IEEE Electron Device Letters, Vol. 9, No. 2, February 1988, p. 100.
- M. Kimata, M. Denda, N. Yutani, S. Iwade, and N. Tsabouchi, <u>A512*512-element</u> <u>PtSi Schottky-barrier IR-CCD image sensor</u>, IEEE J. Solid-State Circuits, Vol. SC-22, No.6, Dec. 1987, pp. 1124-1129.
- H.J. Hovel, <u>Solar cells</u>, Semicond. Semimet., 11 (1975), pp. 112-126, pp. 199-201.
- D.L. Pulfrey and R.F. McOuat, <u>Schottky-Barrier Solar-Cell Calculations</u>, Appl. Phys. Lett., 24 (1974), p. 167.
- J.P. Levin, <u>Theory of Varistor Electronics Properties</u>, Crit. Rev. Solid State Sci., 5 (1975), p. 597.
- IS) Zs. J. Horvath, I. Nemeth-Sallay, B. Szentpali, and K. Kazi, <u>GaAs Schottky</u> <u>Varactors for Linear Frequency Tuning in X-Band</u>, phys. stat. sol. (a) 94 (1986), p. 719.
- M.H. Norwood, and E. Shatz, <u>Voltage Variable Capacitor</u> <u>Tunning A Review</u>,
 Proc. IEEE, 56 (1968), p.788.
- H.S. Veloric, and M.B. Prince, <u>High Voltage Conductivity-Modulated Silicon</u> <u>Rectifier</u>, Bell Syst. Tech. J., 36 (1957), p. 975.
- J.M. Woodall, N. Braslau, and J.L. Freeouf, <u>Contacts to GaAs Devices</u>, Physics of Thin Films, Vol. 13, p. 1987
- K.Y. Tsao, and H.H. Busta, <u>Low Pressure CVD of Tungsten on Polycrystalline and</u> single Crystal Silicon Via the Silicon Reduction, J. Electrochem. Soc., 131(11):2703, November 1984.

- E.K. Broadbent, and C.L. Ramiller, <u>Selective Low Pressure Chemical Vapor</u>
 <u>Deposition of Tungsten</u>, J. Electrochem. Soc., 131(6):1427, June 1984.
- Y. Pauleau, <u>Chemical Vapour Deposition of Tungsten Films for Metallization of</u> <u>Integrated Circuits</u>, Thin Solid Films, 122:243, 1984.
- W.A Bryant, <u>Kinetics of Tungsten Deposition by the Reaction of WF6 and</u>
 <u>Hvdrogen</u>, J. Electrochem. Soc., 125(a):1534, September 1978.
- C.M. Melliard-Smith, A.C. Adams, R.H. Kaiser, and R.A. Kashner, <u>CVD Tungsten</u> for Semiconductor Metallizations, J. Electrochem. Soc., 121(2):298, February 1974.
- M.L. Green, and R.A. Levy, <u>Structure of Selective Low Pressure Chemically</u> <u>Vapor-Deposited Films of Tungsten</u>, J. Electrochem. Soc., 132(5):1243, May 1985.
- C.E. Morosanu, and V. Soltuz, <u>Kinetics and Properties of CVD Tungsten Films on</u> <u>Silicon Substrates</u>, Thin Solid Films, 52: 181, 1978.

- M.T. Schmidt, D.V. Podlesnik, H.L. Evans, C.F. Yu, E.S. Yang, and R.M. Osgood,
 Jr., <u>The Effect of a Thin Ultraviolet Grown Oxide on Metal-GaAs Contacts</u>, J. Vac.
 Sci. Technol. A 6(3), May/Jun 1988, p. 1446.
- Zs. J. Horvath, <u>Evaluation of the Interface State Energy Distribution from</u>
 <u>Schottky I-V Characteristics</u>, J. App. Phys. 63 (3), 1 February 1988, p. 976.
- F. Chekir, C. Barret, and A. Vapaille, <u>A Study of Interface State in Metal-GaAs</u>
 <<u>110> Structures by Schottky Capacitance Spectroscopy</u>, J. Appl. Phys. 54
 (11), November 1983, p. 6474.
- S.D. Mukherjee and C.J. Palmstron, <u>The Thermal Stability of Thin Layer</u> <u>Transition and Refractory Metallisation on GaAs</u>, J. Vac. Sci. Technol., 17 (5), Sept./Oct. 1980, p. 904.
- 30) L.H. Kaplan and F.M. d'Heurle, <u>The Deposition of Molybdenum and Tungsten</u> <u>Films from Vapor Decomposition of Carbonyls</u>, J. Electrochem. Soc.: Solid State Science, May 1970, p.693.

31) S.M. Sze, <u>Semiconductor Devices Physics and Technology</u>, 1985.

- 32) C.Y. Nee, Chun-Yen Chang, T.F. Cheng, and T.S. Huang, <u>An Improved Mo/n-GaAs</u> <u>Contact by Interposition of a thin Pd Layer</u>, IEEE Electron Device Letters, Vol.
 9, No. 6, June 1988, p. 315.
- 33) K. Suh, H.K. Park, and K.L. Moazed, <u>Interfacial Studies of Deposited Thin Films</u> of Refractory Metals on Gallium Arsenide Substrate. Mo-GaAs, J. Vac. Sci. Technol. B, Vol. 1, No. 2, p. 365, 1983.
- P.M. Batev, M.D. Ivanovitch, E.I. Kafedjiiska, and S.S. Simeonov, <u>Schottky</u> <u>Barrier at a Mo-GaAs Contact</u>, Int. J. Electronics, 1980, Vol. 48, No 6, pp. 511-517.
- 35) C.R. Crowell, J.C. Sarace, and S.M. Sze, <u>Tungsten-Semiconductor</u> <u>Schottky-Barrier Diode</u>, Trans.of Metall. Soc. of AIME, Vol. 233, March 1965, p. 478.
- I. Wender and P. Pino, <u>Organic Synthesis via Metal Carbomyls</u>, John Wiley and Sons, p. 40.
- E.H. Rhoderick and R.H. Williams, <u>Metal-Semiconductor Contacts</u>, Clarendon Press, Oxford, 1988.

- 38) Joyce and Neave, Influence of Substrate Surface Conditions on the Nucleation and Growth of Epitaxial Silicon Film, Surface Sci., 1969, 15(1), pp. 1-13.
- 39) Cowley, J. Appl. Phys., 36(10), PP. 3212-20, 1965.
- Thanailakis, <u>Metal Contacts on Ultrahigh Vaccuum Cleaved Silicon</u>, Inst. Phys.
 Conf. Ser. 1974, 22 (Met. -Semicond. Contacts, Proc. Conf.) 59-66.
- Otterloo and Gerritsen, <u>The Accuracy of Schottky Barrier Height Measurements</u> on Clean-Cleaved Silicon, J. Appl. Phys. 1978, 49(2), pp. 723-9.
- 42) Newman et al., <u>Annealing of Intimate Gold-Gallium Arsenide Schottky Barrier</u>.
 <u>Thick and Ultrathin Metal Films</u>, J. Appl. Phys. 1985, 57(4), pp. 1247-51.
- 43) B.L. Smith, J. Appl. Phys. 40(1969), 4675.
- 44) H.B. Michaelson, J. Appl. Phys., 48(1977), 4729

BIOGRAPHICAL NOTE

The author was born 5 January 1963, in Paris, France. In 1968, he attended the American School of Aman, Jordan. In 1969, he attended a private boarding school in Mongeron, Seine et Marnes, France. In 1970, he moved to Varennes-Jarcy, Essones, France, and attended there, grammar school until he was accepted, in 1974, to College Privee de Passy-Buzenval, a catholic boarding school in Rueil et Malmaison, Hauts de Seine, France. In 1978, he attended Lycee de la Folie Saint-James in Neuilly s/r Seine, Hauts de Seine, France, until he received his Baccalaureat S2(Biology) mention assez bien, in 1982. The following year was spent at Clackamas Community College, Oregon City, OR, where he mostly studied Chemistry and Math. In 1983, he was accepted to Reed College from which he graduated in Physics, in May 1986. In January 1987, he started at Oregon Graduate Center a Master of Science in Electrical Engineering, which was completed in May 1989.