FABRICATION AND CHARACTERIZATION OF EMBEDDED GOLD NANOPARTICLES IN METAL CONTACTS FOR SILICON AND SILICON CARBIDE-BASED DEVICES

by

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DEDICATION

This thesis is dedicated to my beloved wife, Maryam.

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In the Name of God, the Compassionate, the Merciful

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TABLE OF CONTENTS

CHAPTER 3 – MATERIALS AND METHODOLOGY

CHAPTER 4 – RESULTS AND DISCUSSION

LIST OF TABLE

LIST OF FIGURE

LIST OF ABREVIATIONS

AD	Aerosol Deposition
AFM	Atomic Force Microscope
AP	Acceleration Potential
APAM	Anodic Porous Alumina Nano-mask
BEEM	Ballistic Electron Emission Microscopy
CBM	Conduction Band Minimum
CND	Colloidal Nanoparticle Deposition
DDSA	Direct deposition self-assembly
DLVO	Derjaguin–Landau–Verwey–Overbeek
DMA	Differential Mobility Analyzer
DTFD	Discontinuous thin film deposition
EF-TEM	Energy Filtered Transmission Electron Microscopy
ETTI	Enhanced Tunneling at Triple Interface
FE	Field Emission
FE-SEM	Field Emission Scanning Electron Microscopy
FIB	Focused Ion Beam
FL	Fermi Level
IBE	Ion Beam Etching
ISBH	Inhomogeneity in Schottky Barrier Height
ITO	Indium Tin Oxide
LEDs	Light Emitting Diodes
MOSFET	Metal-Oxide-Semiconductor Field Effect Transistor
MS	Metal-Semiconductor

NPs	Nanoparticles
PDA	Post Deposition Annealing
PL	Photoluminescence
RBS	Rutherford Backscattering Spectrometry
RCA	Radio Corporation of America
RIE	Reactive Ion Etching
RPM	Rate Per Minute
SBD	Schottky barrier Diode
SBH	Schottky Barrier Height
SBM	Schottky Barrier Height Map
SEM	Scanning Electron Microscopy
SPA	Semiconductor Parameter Analyzer
STM	Scanning Tunneling Microscope
TE	Thermionic Emission
TEM	Transmission Electron Microscope
TFE	Thermionic Field Emission
WF	Work Function
XRD	X-ray Diffraction Spectroscope

LIST OF SYMBOLS

%	Percentage
[ ]	Concentration
<	Less than
>	More than
°	Degree
°C	Degree Celsius
A	Ampere
A**	Richardson constant
cm	Centimetre
d	Thickness
E_{00}	Tunneling probability
E_C	Conduction band minimum
E_F	Fermi level energy
eV	Electron volt
E_V	Valence band maximum
E_{Vac}	Vacuum energy level
g	Gram
K	Kelvin
m^*	effective mass
min	Minute
ml	Milliliter
mm	Millimeter
$N_{a,d}$	acceptor or donor concentration

nm	Nanometer
R_0	NPs Radius
rpm	Rate per minute
s	Second
T	Temperature
V	Voltage
V_a	Applied bias
V_{bb}	Diffusion potential (w)
V_T	Tunnel Voltage
w	Depletion width (nm)
wt %	Weight percent
z	Distance from the surface of semiconductor
Δ	Difference in Schottky Barrier Height (eV)
ε_s	Dielectric constant of semiconductor
λ	Wave length
ρ	Contact Resistivity (Ω cm^2)
Φ	Work Function (eV)
Φ_b	Schottky Barrier Height (eV)
Φ_m	Metal Work Function (eV)
Φ_s	Semiconductor Work Function (eV)
χ_s	Electron Affinity (eV)

LIST OF PUBLICATIONS

International Peer-Reviewed Journals (ISI Indexed):

1. Mohammad Saleh Gorji, Khairunisak Abdul Razak, Kuan Yew Cheong, "*Gold nanoparticles deposited on linker-free silicon substrate and embedded in aluminum Schottky contact*". Journal of Colloid and Interface Science, 2013. 408: p. 220-228. (**IF: 3.17**).

2. Mohammad Saleh Gorji, Khairunisak Abdul Razak, Kuan Yew Cheong "*Embedded Au Nanoparticles in Al Schottky Contacts on Si: Electrical Characteristics*", *Journal of Applied Physics* (**IF: 2.21**), AIP, (Submitted).

3. Mohammad Saleh Gorji & Kuan Yew Cheong "*Embedded Nanoparticles in Schottky and Ohmic Contacts: A Review*", *Critical Reviews in Solid State and Materials Sciences* (**IF: 5.95**), Wiley, (Submitted).

4. Mohammad Saleh Gorji & Kuan Yew Cheong ""*Au Nanoparticles Embedded at the Interface of Al/4H-SiC Schottky Contacts for Current Density Enhancement: Electrical Characteristics*", *Applied Physics A* (**IF: 1.54**), Springer, (Submitted).

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PEMBUATAN DAN PENCIRIAN NANOPARTIKEL EMAS TERBENAM KE DALAM SENTUHAN LOGAM UNTUK PERANTI BERASAS SILIKON DAN SILIKON KARBIDA

ABSTRAK

Penerapan logam nanopartikel (NPs) ke dalam sentuhan logam di antara muka dengan semikonduktor adalah kaedah alternatif untuk mengubahsuai ketinggian halangan Schottky (SBH) dalam sentuhan elektrik dan membolehkan adaptasi langkah-langkah pemperosesan menjadi lebih mudah. Diod penghalang Schottky bersentuhan aluminium (Al) tertanam dengan emas (Au) NPs pada silikon (Si) jenis n- dan p- serta silikon karbida (4H- SiC) substrat telah direka, malah ciri-ciri fizikal dan elektrik mereka telah disiasat. Berdasarkan kajian hasil pengukuran permukaan sentuhan sudut ke atas Si dan nilai-nilai zeta-potensi negatif pembenihan 20 nm Au NPs, satu pendekatan alternatif telah dicadangkan untuk mendepositkan Au NPs pada pemaut bebas n- dan p-Si substrat dengan menggunakan teknik putaran salutan. Ketumpatan NPs pada n-Si adalah lebih tinggi dari p-Si (ditentukan oleh mikroskop pengimbas elektron), disebabkan oleh perbezaan ciri-ciri permukaan n- dan p-Si. Analisa arus-voltan diod Al/Si menunjukkan peningkatan dalam ketumpatan arus diod dalam kedua-dua arah pincang kerana kesan peningkatan medan elektrik tempatan NPs dan SBH berkurang (0.11 eV untuk n- dan 0.05 eV untuk p-Si). Keputusan sefat elektrik kemudiannya dikaitkan dengan sifat-sifat struktur Al/Si (ditentukan oleh mikroskop transmisi elektron). Kepadatan lebih tinggi Au NPs yang bersaiz 5 dan 10 nm telah dienapkan di permukaan SiC dengan menggunakan teknik pengasidan dengan HF. Diod Al/4H-SiC menunjukkan peningkatan yang besar

dalam penurunan SBH (0.09 eV untuk n- dan 0.24 eV untuk p- 4H- SiC) dan dengan itu ketumpatan arus terus di samping mengekalkan ciri-ciri penyearah pincang songsang. Untuk menentukan punca peningkatan medan elektrik tempatan adalah dengan kehadiran NPS di logam- semikonduktor, model ketakhomogenan Tung dalam SBH (ISBH) dan model tiga kali ganda antaramuka terowong dipertingkatkan (ETTI) telah digunakan. NPs bersaiz kecil adalah factor penting dalam kedua-dua model. Faktor-faktor lain seperti saiz NPs dan perbezaan antara SBH Au/Al dan Si/Si ($\Delta = \Phi_{b\,(Al\,/\,Si)} - \Phi_{b\,(Au\,/\,Si)}$) dalam model ISBH dan saiz dan fungsi kerja Al/Au (Φ_{Al} - Φ_{Au}) dalam model ETTI. Dalam sistem Al/Si, magnitud Δ adalah lebih kecil (0.31 eV untuk n -Si dan 0.24 eV untuk p-Si) berbanding dengan perbezaan fungsi kerja antara Au/Al (Φ_{Al} - $\Phi_{Au} \sim$ 1 eV) dan dengan itu peningkatan medan elektrik terutamanya disebabkan oleh kesan peningkatan tiga kali ganda terowong antara muka. Dalam sistem Al/4H-SiC oleh kerana magnitud Δ (0.77 eV untuk n-SiC dan 0.45 eV untuk p-Si) juga tinggi secara relatif, kedua-dua model dijangka menyumbang kepada peningkatan medan elektrik.

FABRICATION AND CHARACTERIZATION OF EMBEDDED GOLD NANOPARTICLES IN METAL CONTACTS FOR SILICON AND SILICON CARBIDE-BASED DEVICES

ABSTRACT

Embedding metal nanoparticles (NPs) into metal contacts, at the interface with semiconductor, is an alternative method for modification of Schottky barrier height (SBH) in electrical contacts and offers a tremendous simplification and adaptation in processing steps. Schottky barrier diodes with aluminum (Al) contacts embedded with gold (Au) NPs on n- and p-type silicon (Si) and silicon carbide (4H-SiC) substrates were fabricated and their physical and electrical characteristics were investigated. Based on the studies on Si surface contact angle measurement and the negative zeta-potential values of seeded growth 20 nm Au NPs, an alternative approach was proposed to deposit Au NPs on linker-free n- and p-Si substrates using spin-coating technique. Density of NPs (determined by scanning electron microscope) on n-Si was substantially higher than p-Si which was due to the differences in surface properties of n- and p-Si. Current-voltage analysis of diodes revealed an increase in current density in both bias directions due to NPs local electric field enhancement effect and SBH lowering (0.11 eV for n- and 0.05 eV for p-Si). The electrical results were then correlated to the structural properties of Al/Si (determined by transmission electron microscope). Higher density of 5 and 10 nm Au NPs were deposited on SiC surface by using acidification technique with diluted HF. Al/4H-SiC diodes showed great improvement in SBH lowering (0.09 eV for n- and 0.24 eV for p-4H-SiC) and hence forward bias current density elevation while maintaining the rectification properties in reverse bias. To determine the source of

local electric field enhancement due to the presence of NPs at the metal-semiconductor, Tung's model of inhomogeneity in SBH (ISBH) and enhanced tunnelling at triple interface model (ETTI) were invoked. Small size of NPs is the key factor in both models. Other factors are the difference between the SBH of Au/Si and Al/Si ($\Delta = \Phi_{b\ (Al/Si)} - \Phi_{b\ (Au/Si)}$) in ISBH model and Al/Au work function (WF) difference ($\Phi_{Al} - \Phi_{Au}$) in ETTI model. The potential and electric field distribution were also calculated. In Al/Si system the magnitude of Δ was smaller (0.31 eV for n-Si and 0.24 eV for p-Si) compared with the WF difference of Au/Al (~ 1 eV) and hence the electric field enhancement was mainly attributed to ETTI model. In Al/4H-SiC system since the magnitude of Δ (0.77 eV for n-SiC and 0.45 eV for p-Si) were also relatively high, both models were expected to attribute to the electric field enhancement.

CHAPTER 1 -

INTRODUCTION

1.1 Background

Electrical contacts are fundamental to semiconductor devices, as gates and contacts in diodes, transistors, etc., and are one of the most important parts of modern integrated circuitry (Cohen and Gildenblat, 1986, Ghate, 1982). In order to understand and predict the properties of electrical contacts it is essential to comprehend the semiconductor surface and interface chemistry and physics prior and upon the intimate connection and coupling with the contact material. In general, when a material (a metal in particular) is put into an intimate contact with a semiconductor, the energetic balance is disturbed at the metal-semiconductor (MS) interface due to the difference in the energy levels of the metal and the semiconductor. To restore the balance, charge carriers (electrons or hole) would begin to redistribute and hence the atoms at the semiconductor become ionized and depleted of charge carriers. The depleted region is so called depletion region, depletion layer, or space charge region. This process continues until the potential energy barrier, which is formed due to the presence of ionized atom and formation of an electric field, would prevent further charge transfer across the MS interface. The thickness of the depletion region is defined as the depletion width (w).

Figure 1.1 (a-d) is a typical representation of energy band diagrams of metal and n- and p-type semiconductors before and after the intimate contact. The vacuum energy level (E_{Vac}), conduction band minimum (E_C), valence band maximum (E_V), and Fermi level (FL) energy (E_F) have been defined. FL is a measure of the probability of occupancy of allowed energy states by electrons or hole.

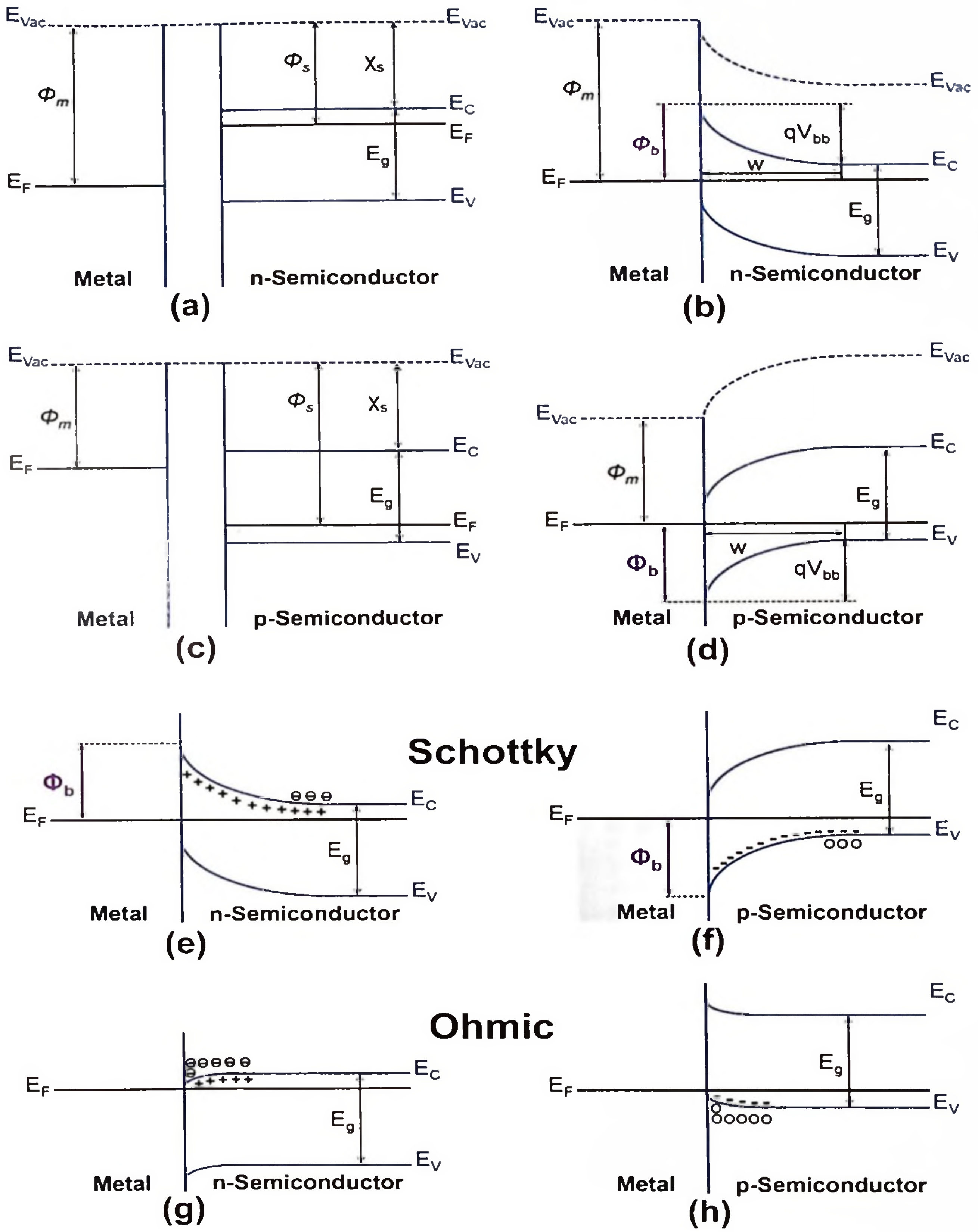

Figure 1.1: Typical representation of energy band diagrams before (a, c) and after (b, d) the intimate contact between a metal and respectively n- and p-type semiconductors. Based on the potential energy difference (Φ_m - Φ_s) Schottky (a, b) or Ohmic (c, d) contacts are formed on n- and p-type semiconductors, respectively.

Φ_m is the work function (WF) of the metal which is a measure of the required energy to remove an electron from FL of the metal. The WF of the semiconductor is also Φ_s. However, in semiconductors a more useful quantity, i.e. electron affinity χ_s, is often used which is the difference between the vacuum energy level (E_{Vac}) and the bottom of the conduction band (E_C).

Based on the value of potential energy difference (Φ_m - Φ_s), the barrier could rectify the current, which in this case is termed Schottky (rectifying) contact (Figure 1.1 (e) – (f)). But, when there is a minimum barrier or the barrier is non-rectifying (Anderson and Anderson, 2005) the term "Ohmic contact" is applied to the electrical contact (Figure 1.1 (g) and (h)).

Most metals form a rectifying Schottky contact on both n- and p-type semiconductors with a specific value of SBH (Φ_b). The SBH is ideally determined by a relationship known as "Schottky-Mott limit" (Schottky, 1939, Mott, 1939), which is the difference between the WF of a metal (Φ_m) and electron affinity (χ_s) of a semiconductor (n-type). The experimental results on many semiconductors, however, indicate a weak dependency or even independency of SBH to Φ_m (Porter and Davis, 1995). This deviation from Schottky-Mott limit has led to the development of another theory based on MS interface energy states. At the surface of a semiconductor, atoms have unsaturated dangling bonds. These unsaturated bonds create allowed energy states within the band gap (E_g) at the surface of the semiconductor. When these energy states are present at the interface of a semiconductor and a metal they are referred to as "interface states". The relationship between the SBH and interface states is known as "Bardeen limit" (Bardeen, 1947). Bardeen found that the number of interface states can be so high that would lead to pinning of FL position at the semiconductor surface and making SBH completely independent of Φ_m (Colinge and Colinge, 2005, Brillson, 1993). It should be noted that the band bending in Schottky-Mott model is entirely due to the difference in Φ_m and Φ_s. But in case the FL in semiconductor is pinned, as the metal is brought into contact with the semiconductor no change takes place within the depletion region of semiconductor. This is because the charge in interface states would fully accommodate the potential energy difference (Φ_m - Φ_s). The practical relationship between SBH and Φ_m, however, is usually somewhere between the two limits which has been developed and modified by other researchers (Tung, 2000a, Tung, 2001, Sullivan et al., 1991). Another source of the deviation from ideal Schottky diode is the image force lowering effect on SBH. When an electron approaches from semiconductor to a specific distance from the metal contact a positive charge will be induced in the metal part. The existence of the positive charge at the mirror image location of the electron will form an electrostatic force which is called image force and the SBH will be lowered by this exerted force (Achuthan and Bhat, 2006).

Modification of the electrical properties of Schottky and Ohmic contacts is directly linked to the MS interface properties and in particular the band bending and Schottky barrier formation at the MS interface. Thus, engineering and modification of SBH is the key to design and fabricate electronic and optical devices with desired electrical properties.

In Schottky contacts the purpose of SBH modification can be both increasing the SBH, to improve rectification properties, and reducing the SBH, to reduce on-state voltage drop in forward bias (V_F) while maintaining the rectification properties in reverse bias. The current-voltage (I-V) characteristics of a practical Schottky contact are shown in Figure 1.2 (a). Inset is the logarithmic representation of the I-V.

The corresponding energy band diagrams of Schottky contacts when a voltage is applied in forward (F) and reverse (R) bias directions are also demonstrated in Figure 1.2 (b) and (c), respectively.

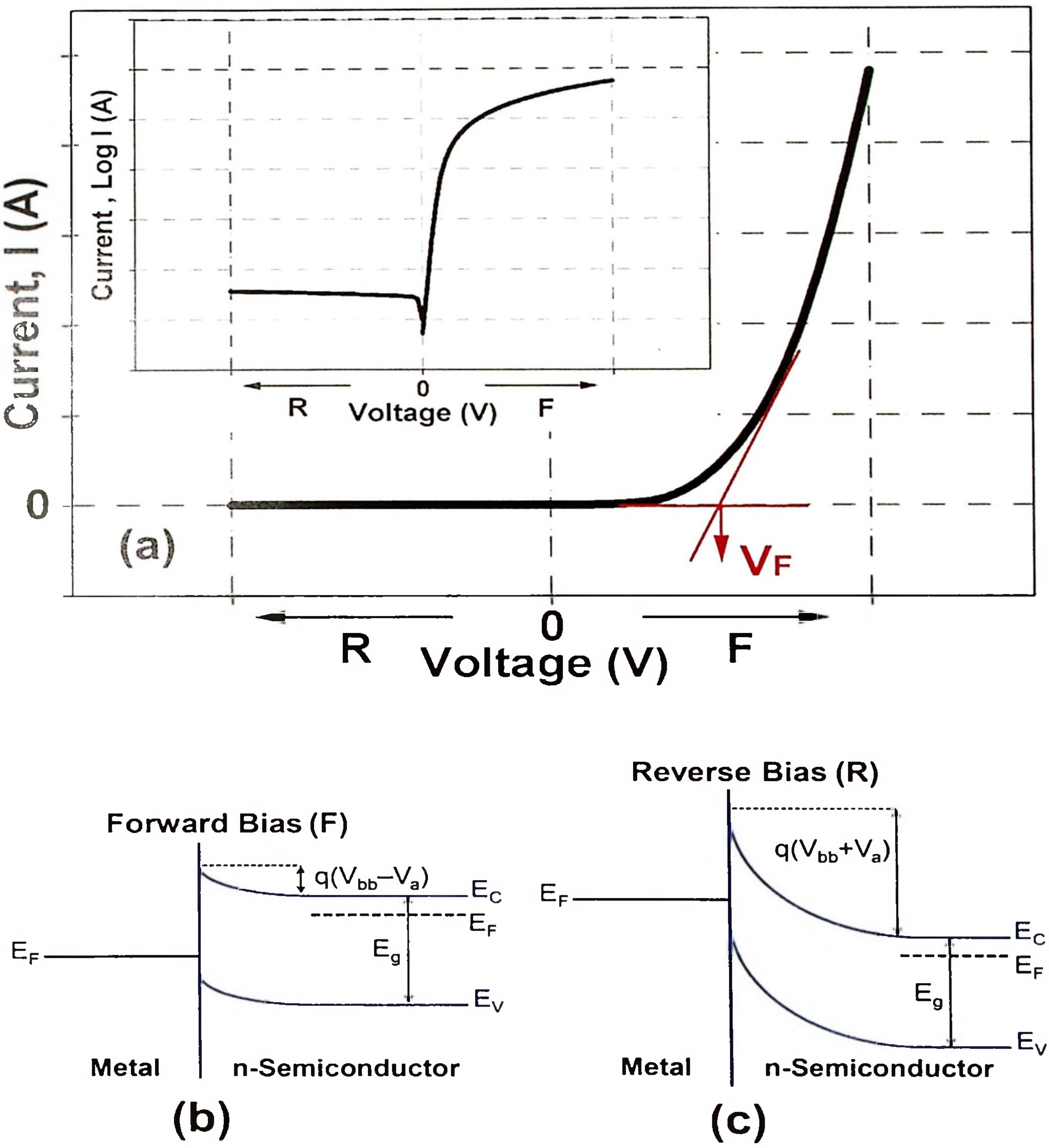

Figure 1.2: I-V characteristics of a Schottky contact (a); as well as its corresponding energy band diagrams in forward (b) and reverse (c) bias directions.

In forward bias the potential barrier decreases with applied voltage and electrons in the semiconductor conduction band receive enough potential energy to effectively surmount the potential energy barrier from semiconductor to metal. Thus, a large number of electrons flow and their number increase exponentially with the applied voltage (V_a). In reverse bias, the potential barrier increases with applied voltage and hence negligible number of electrons can flow from semiconductor to metal.

In Ohmic contacts the lowest possible resistivity for current conduction to and from the semiconductor is required which can be achieved by reducing the overall SBH. In practical Ohmic contacts the current injection in and out of semiconductor should happen with lowest possible resistance and the I-V characteristics should be linear in both bias directions. Figure 1.3 (a) and (b) depict the typical linear and logarithmic I-V characteristics of Ohmic and semi- (or quasi-) Ohmic contacts. Ohmic contacts are often evaluated based on the value of contact resistivity (ρ), which is a measure of all the factors, including the SBH, that contribute to the current conduction at MS interface. By decreasing the contact resistivity current conduction in both directions increases and the electrical contact characteristics transform from Schottky to semi-Ohmic or Ohmic behavior. A practical Ohmic contact should have a low contact resistivity (ρ) with a small voltage drop across the contact when compared with the active device region (Dobbs et al., 1977, Blank and Gol'dberg, 2007). The typical values of contact resistivity are in the order of 10^{-5} Ω cm^2.

In the process of SBH modification, selection of an appropriate material may very well seem to be the easiest option to acquire a particular SBH. This approach becomes challenging as finding a suitable contact material is often limited by the number of available and feasible materials and also considerations of cost, processing step and temperature, etc. As a result, SBH is often modified without changing the material itself, by tuning the MS interface properties instead.

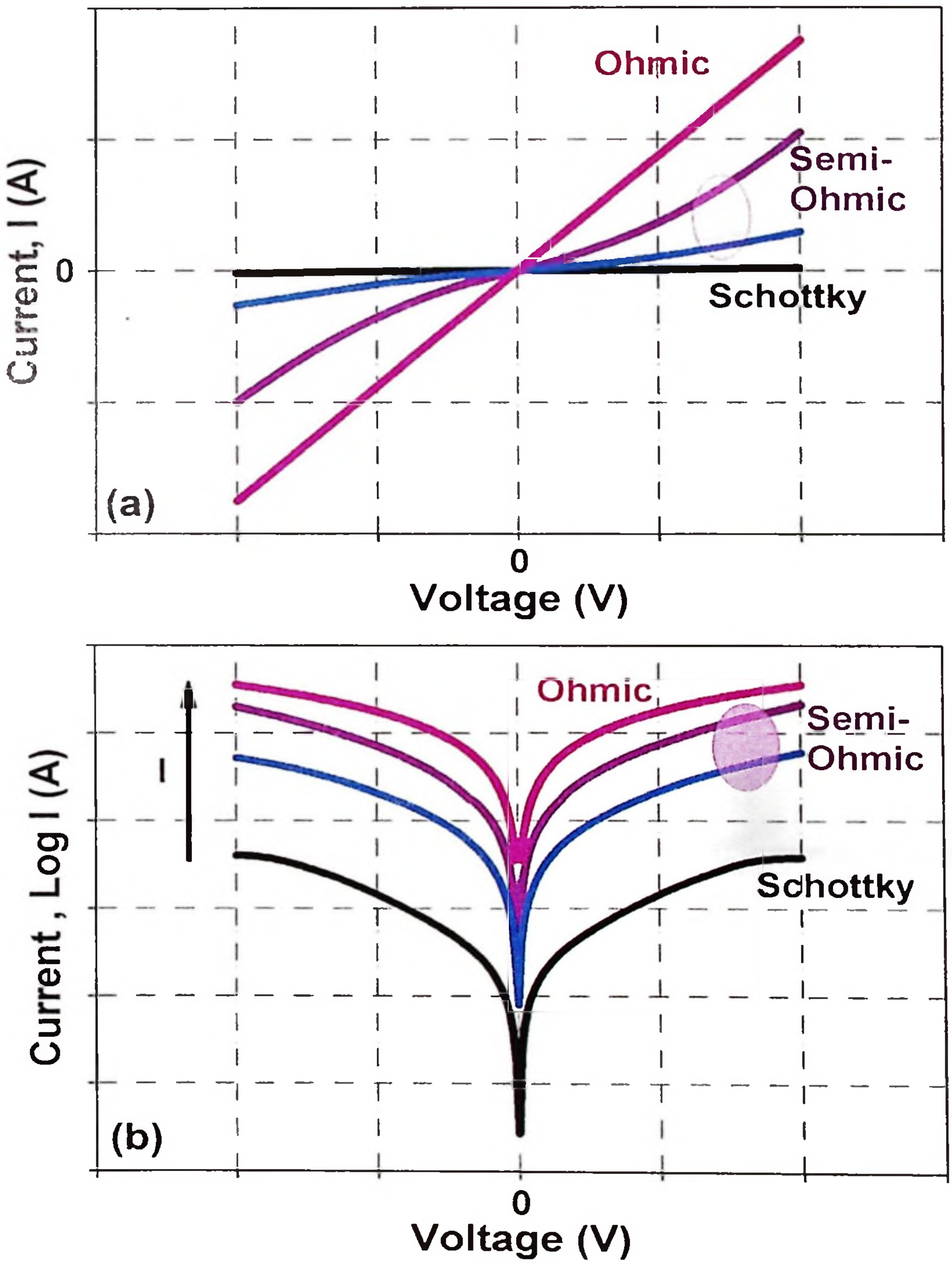

Figure 1.3: Typical linear (a) and logarithmic (b) I-V characteristics of Ohmic and semi-Ohmic contacts. Transformation of Schottky to semi-Ohmic (marked by pink oval) or Ohmic behavior is due to the reduction of contact resistivity.

Other than changing the contact material itself, measures that have been taken place to modify the Schottky barrier in Schottky and Ohmic contacts can be mainly divided into two categories: Pre-contact deposition and post-contact deposition treatments.

Post-contact deposition treatment mainly consists of a post deposition annealing (PDA) step that leads to creation of an interfacial compound at the MS interface with unique desired properties. PDA steps are strictly temperature sensitive. For example, the PDA of Ni/n-4H-SiC Schottky contacts at higher than 600°C results in the formation of Ni_2Si at the interface, while maintaining the Schottky behavior. However, at PDA processes higher than 900°C a graphite phase is formed under the Ni_2Si layer which transforms the Schottky into Ohmic contact (Han et al., 2001).

Pre-deposition treatments can also be carried out on substrate itself, before the deposition of contact material, to change and create new electronic states at the surface of semiconductor, with processes such as surface passivation (Jia and Qin, 1990, Tao et al., 2003), native oxide thickness variation (Siad et al., 2004, Altindal et al., 2006) and removal (Miyawaki et al., 1990), or insertion of organic/inorganic materials (thin films (Soylu et al., 2011, Pakma et al., 2008) or monolayers of atoms (Wang et al., 2009)) at the MS interface. The inserted layer can effectively alter (promote or diminish) the current conduction through the MS interface based on the application of contact and the nature of the contact and semiconductor materials (Zheng et al., 2013, Tredgold and El-Badawy, 1985). One common pre-deposition treatment, which is being used in majority of actual Ohmic contacts in electronic devices, is increasing the doping concentration near the surface of the semiconductor. This will narrow the Schottky barrier width and facilitate the direct tunneling of the charge carriers through the barrier (Anderson and Anderson, 2005).

The above mentioned approaches that are being applied for modification of electrical contacts have their own merits and drawbacks. The drawbacks are mainly associated with the limitations in controlling the semiconductor surface properties in pre-contact deposition treatments or the MS interface undesirable changes in post-contact deposition treatments such as undesirable and unexpected reactions at MS interface due to the semiconductor surface contamination and poor metal deposition techniques (Ghate et al., 1977, Blair and Ghate, 1977, McCarthy, 1970). Another common device failure especially in aluminium (Al)/silicon (Si) system is thermo-migration (spiking), which is basically the mass transport (Si atoms into Al and vice versa) across the interface during the annealing process (Cohen and Gildenblat, 1986). Formation of an undesirable thin p-n junction layer at the MS interface due to the unintentional doping of the semiconductor with the opposite dopant is another device failure. In this phenomenon, diffusion of contact metal atoms (with opposite doping property) to the semiconductor during the annealing, can alter the effective SBH value. For example, diffusion of Al atoms (with three valence electrons) into n-Si during Al/n-Si PDA step (Vaidya and Sinha, 1982).

To address the above-mentioned issues and constrains of the conventional methods of electrical contact fabrication, a modern and novel scheme was introduced to modify the Schottky barrier without the need to make substantial alteration of semiconductor surface properties, changing its near-surface doping concentration, or any post deposition heat treatments of the contact material. In this method which is based on the local electric field enhancement effect, the effective SBH is modified and reduced by incorporation and embedding of nano-sized particulates (referred to as "nanoparticles (NPs)" throughout the thesis) in contact materials at the MS interface (Olbrich et al., 1998, Narayanan et al., 2000). This contact structure is being referred to as "nanostructured contact" hereafter. This term should not be confused with nano-scaled contacts on nanomaterials such as nanotubes, nanorods, nanowires, graphene, etc. as their electrical behavior is often fundamentally different because of their special geometries (Léonard and Talin, 2011). Figure 1.4 (a) shows the cross-sectional schematics of the nanostructured contacts with embedded NPs at the MS interface.

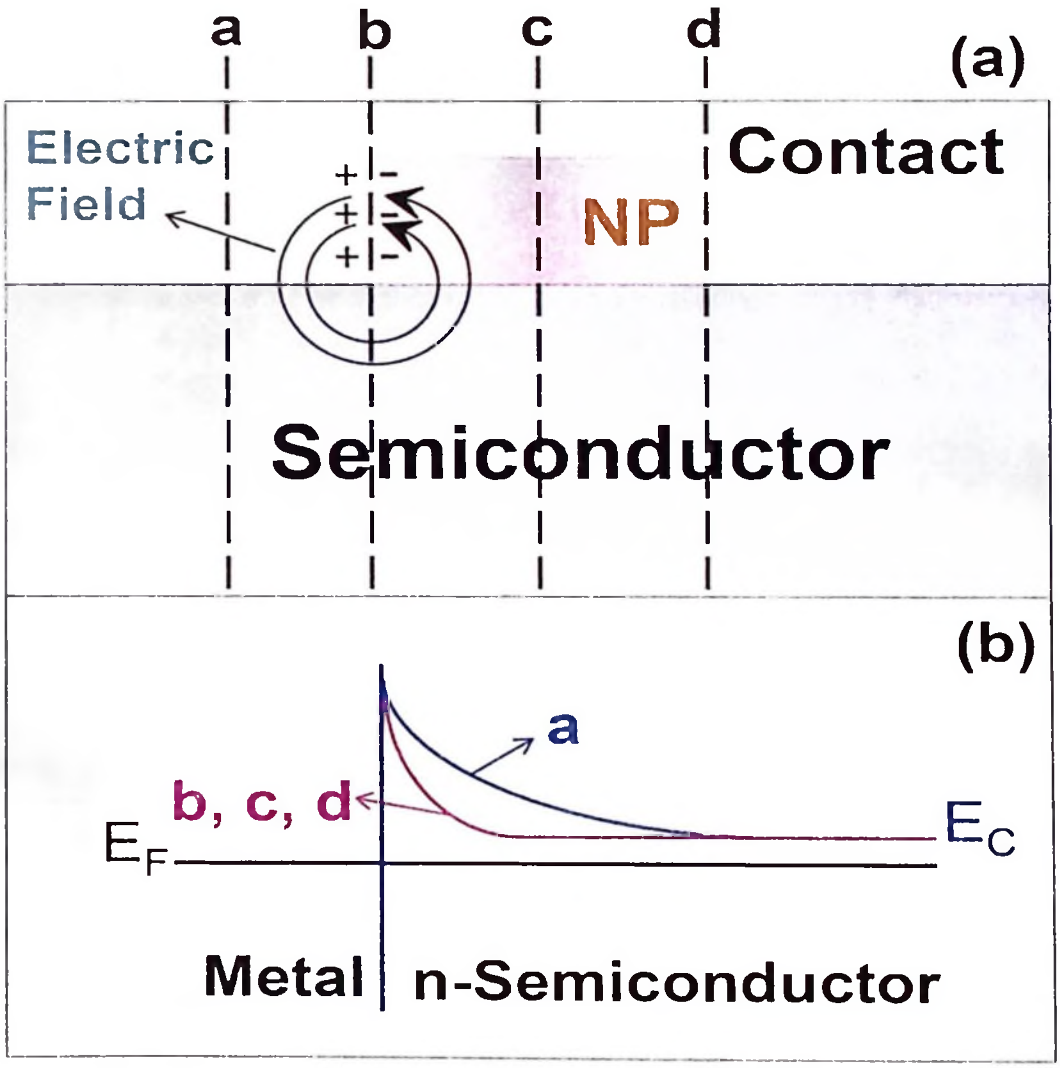

Figure 1.4: Cross-sectional schematics of the nanostructured contacts with embedded NPs at the MS interface (a) and corresponding band structure changes due to the effect of NPs along a-d dash-lines (b). The barrier has become thinner along dash-lines b and d (based on ETTI model) and dash-line c (based on ISBH model) as opposed to normal band structure along dash-line a.

The effect of the embedded NPs in a contact material is most often explained by the Tung's model of inhomogeneity in SBH (ISBH) (Tung, 1991), and the model of enhanced tunneling at nanoparticle/semiconductor/metal contact triple interface (ETTI) by Narayanan et al., (2000). Both ISBH and ETTI models have been discussed in details in section 2.7. The presence of NPs at the interface would create an electric field, strong enough to overcome the electric field in the depletion region of semiconductor, which would locally thin the Schottky barrier. Thus, the tunneling of charge carrier through the barrier is enhanced that would eventually contribute to the current conduction enhancement and the overall SBH lowering.

Figure 1.4 (b) corresponds to the band structure changes due to the effect of NPs along dash-lines a-d. The barrier has become thinner along dash-lines a and d (based on ETTI model) and dash-line c (based on ISBH model) as opposed to the normal band structure along dash-line a. Discussions on the effect of NPs on current conduction and ISBH and ETTI models can be found in sections 2.5 and 2.6, respectively.

Different types of NPs have been previously embedded in different contact materials to form nanostructured Schottky and Ohmic contacts on variety of substrates (i.e. Si, Ge, SiC, GaN, $GaAs_{67}P_{33}$, and InP). Fabrication process of these nanostructured contacts mainly consists of two main steps: deposition of NPs on the substrates and subsequently deposition of contact material on top of NPs. In order to deposit NPs on substrates substrate, as the first fabrication step, different techniques have been adopted including, aerosol deposition (Lee et al., 2002), direct deposition self-assembly (Kang et al., 2012b, Kang et al., 2012a, Ruffino et al., 2010b, Ruffino et al., 2010a), discontinuous thin film deposition (Olbrich et al., 1998, Olbrich et al., 1997), and deposition through anodic porous alumina nano-mask (Sohn et al., 2004c, Sohn et al., 2004b) which have also been used for realization of NPs on different substrates and subsequent fabrication of nanostructured contacts as presented in Figure 1.4 (a).

1.2 Problem Statement

From the standpoint of NPs deposition technique, in all the methods mentioned above, NPs are being synthesized and deposited directly onto the substrate during the fabrication procedure. There are some drawbacks and limitations in application of each of these techniques. Limitations such as:

- Controlling and optimization of the shape, size, and uniform distribution of NPs in discontinuous thin film deposition.
- Lengthy processing steps for deposition of NPs in aerosol deposition method that requires several machines connected in a sequential order.
- Fabrication, placement and reliability of the anodic porous alumina nano-mask, as well as, controlling the NPs size and distribution when deposited through the nano-mask.
- The requirement of a heat treatment process for the fabrication of NPs via direct deposition self-assembly technique that can affect the substrate properties or cause some degree of reaction between the NPs and substrate.

To address some of the issues affiliated with synthesis and deposition of NPs during the nanostructured contact system, in this work, colloidal Au NPs have been used for the first time for nanostructured contact fabrication. One of the main advantages of colloidal Au NPs is the availability of commercial Au NPs in different sizes and densities (i.e. the number of NPs per mililiter). This makes it possible to deposit NPs with specific size and shape onto the substrate by using an appropriate deposition technique. Polymeric linker molecules are often used to adhere the NPs to the substrates. However, since these linker molecules are not removable afterward and would contribute to the conduction mechanism which is not desirable. As a result, for the deposition of Au NPs on linker-free Si substrates by spin-coating technique a new approach based on surface properties of n- and p-Si was introduced. For the deposition of Au NPs on linker-free 4H-SiC substrates, in order to further increase the density of NPs (i.e. the number of NPs per unit area) on the substrates acidification technique (O'Reilly et al., 2012, Woodruff et al., 2007) was adopted.

From the point of view of the electrical characteristics of the nanostructured contact systems, majority of the studies in the literature mainly focus on the adoption of one model to explain the effect of embedded NPs which has proven to be inadequate. For example, the theoretical calculated results predicted by ISBH model have exhibited a usually less than what is experimentally observed for Schottky barrier lowering (Lee et al., 2002). In some studies (Lee et al., 2002, Kwak et al., 2006) the inconsistency is attributed to the effect of ETTI model without a solid argument that integrates or correlates the two models. In this work, Au NPs and Al contact combination was selected for the first time to fabricate nanostructured contacts on both Si and 4H-SiC substrates. Au NPs are the most available and well-studied colloidal NPs. Al is also still one of the most frequently used materials in contact fabrication in electronic circuitry. Apart from the availability and well-defined properties, Au and Al have a relatively high WF difference (~ 1 eV) which is a key factor in nanostructured contact efficiency. Hence, their selection as the contact combination makes it possible to define the dominating model which can best describe the experimentally observed SBH lowering due to the embedded NPs in Si-based diodes. In addition, in 4H-SiC-based diodes, Au NPs/Al contact system effectively reduces the SBH and at the same time maintains the rectification properties of diodes in reverse bias.

1.3 Objectives of the Research

The main objective of this research is to investigate the effect of Au NPs in SBH lowering of Au NPs/Al nanostructured contacts on both Si and 4H-SiC substrates. With this main objective, the following aspects are to be achieved:

1. To investigate the effect of surface properties of n- and p-Si and also the effect of multiple depositions of Au NPs by spin-coating on the final density of Au NPs on Si substrates.
2. To study the effect of the density of Au NPs in SBH lowering of Au NPs/Al contact system on Si substrates.
3. To investigate the effect of surface morphology of n- and p-type 4H-SiC substrates in the density of deposited Au NPs, with two different sizes, by using the acidification method.
4. To investigate the effect of the size of Au NPs in the SBH lowering of Au NPs/Al contact system on 4H-SiC substrates.

1.4 Scope of the Research

In this study, two different types of Au colloidal NPs with different sizes have been used for deposition on Si and 4H-SiC substrates: Seeded growth Au NPs reduced by hydroxylamine with the average size of 20 nm and the solution pH of around 3.2 were deposited on Si substrates by spin-coating technique and their adhesion, distribution and density were comprehensively studied. The mentioned size of NPs is the average diameter (d) of NPs but when required to use the radius instead (for potential and electric field calculations), the NPs size will be specified by R_0. Commercial citrate stabilized Au NPs with sizes of 5 and 10 nm were deposited by acidification method with diluted HF to increase the density of NPs on substrates.

Au NPs/Al contact combination was fabricated on both n- and p-Si and 4H-SiC substrates and their physical and electrical characteristics were comprehensively studied by field-emission scanning electron microscope (FE-SEM), Goniometer, energy-filtered transmission electron microscope (EF-TEM) and semiconductor parameter analyzer (SPA).

1.5 Thesis Outline

This thesis is organized and divided into five chapters. **Chapter 1** provides an overview of current issues in fabrication of electrical contacts on Si and 4H-SiC substrates and challenges in modification of SBH of the contacts and the effectiveness of nanostructured contact systems as an alternative method. Subsequently the current research objectives and the scope of study are further elaborated. **Chapter 2** covers the detailed literature review, which covers two main areas of NPs deposition techniques for fabrication of nanostructured electrical contacts and the physical modeling and interpretation of the structures and their practical applications. In **chapter 3** systematic methodology of the research is presented. **Chapter 4** is the comprehensive elucidation and discussion of the obtained results. **Chapter 5** summarizes this study and its conclusions. This chapter also includes the recommendations for future works.

CHAPTER 2 -

LITERATURE REVIEW

2.1 Overview

The purpose of this literature review is to bring fundamental understanding of the effect of embedded NPs in contact materials. The main scope of this review is limited to the straightforward two-step fabrication processes: NPs deposition on the semiconductor substrate followed by the deposition of the capping contact metal without any post contact deposition heat treatments. The summary of the studies that used the two-step processing for the fabrication of nanostructured contacts is presented in Table 2.1. This table is intended to highlight the main aspects of previous attempts on development of Schottky and Ohmic contacts with embedded NPs. The literature review is comprised of four main parts:

1. NPs deposition techniques.
2. Practical application and reliability of NPs in Schottky and Ohmic contacts.
3. Physical interpretation of NPs effect on electrical properties of contacts.
4. Nanostructured contacts with non-metal NPs or non-metal contacts.

After a brief introduction of Si and SiC substrates in section 2.2, different techniques for NPs deposition are introduced and their advantages and disadvantages are discussed (section 2.3). Second part is the review of the performance and reliability of Schottky and Ohmic contacts embedded with NPs (sections 2.4 and 2.5). In the third part, studies on the NPs effect on electric field enhancement and subsequent influence in current conduction mechanism by invoking two main models of ISBH and ETTI are critically reviewed (sections 2.6 and 2.7). Finally, the state of other nanostructured contacts with non-metal NPs or non-metal contacts on Si and SiC are reviewed (sections 2.7).

Table 2.1: Summary of the studies on Schottky and Ohmic contacts embedded with NPs and fabricated through a two-step process.

Substrate	Contact metal	Embedded NPs	Deposition technique	Applied physical model	Electrical contact type	Focus of the Study	Ref.
InP	Au	Ag	AD	ISBH	Schottky/Ohmic	Electron transport properties	Anand et al. 1996
$GaAs_{67}P_{33}$	Au	Co	DTFD	ISBH	Schottky	Experimental verification of the pinch-off effect	Olbrich et al. 1997
$GaAs_{67}P_{33}$	Au	Co	DTFD	ISBH	Schottky	The origin of the integral barrier height	Olbrich et al. 1998
Si	W/WSi_2	Au	DDSA	ETTI	Ohmic	Reduction of contact resistivity	Narayanan et al. 2000
SiC	Ti	Au	AD	ISBH	Schottky	Reduction of Schottky barrier height	Lee et al. 2002
GaN	Ni	Pt, Au, Al	APAM	ISBH	Schottky/Ohmic	Electrical properties of Ni contacts	Sohn et al. 2004a
GaN	Ni	Au	APAM	ISBH	Ohmic	Effect of Au-nanodots on Electrical Properties	Sohn et al. 2004b
GaN	Al	Pt	DDSA	ISBH/ETTI	Ohmic	High-reflectivity and Ohmic contact improvement on p-GaN	Kim et al. 2006
SiC	Pd	Au	DDSA	ISBH	Schottky	Electrical properties of the diode	Ruffino et al. 2010a
SiC	Pd	Au	DDSA	ISBH	Schottky	Effect of NPs radius on the electrical properties	Ruffino et al. 2010b
SiC	Ni	Au	DDSA	ISBH	Schottky	Effect of annealing on the contacts embedded with NPs	Kang et al. 2011
SiC	Ni	Au/Ag	DDSA	ISBH	Schottky	Schottky barrier height modification	Kang et al. 2012a
SiC	Ni	Au/Ag	DDSA	ISBH	Schottky	Effect of embedded NPs and doping concentration	Kang et al. 2012b
Ge	Au	Ti	DDSA	ETTI	Ohmic	Ohmic contacts on both n- and p-type Ge	Kishore et al. 2012

* Aerosol deposition (AD); Discontinuous thin film deposition (DTFD); Anodic porous alumina nano-mask (APAM); Direct deposition self-assembly (DDSA);
**Inhomogeneity in Barrier Height (ISBH); Enhanced Tunneling at Triple Interface (ETTI)

2.2 Si and SiC

Si with its superior physical and technological advantages over other types of semiconductors is still the most prevailing semiconductor in electronic device industry. Si is an abundant material with low-cost purification and crystallization methods (Brillson, 1993). It has atomic number of 14 with 4 valence electrons and with diamond crystal structure and its relatively strong covalent bonds makes it suitable for mechanical handling and fabrication processing as well. Single crystal Si substrate with high purity is still the most commercially available semiconductor. Figure 2.1 is the 3-dimentional (3D) representation of a Si crystal structure with defined lattice constant (a) of around 0.54307 nm (El-Kareh, 2009).

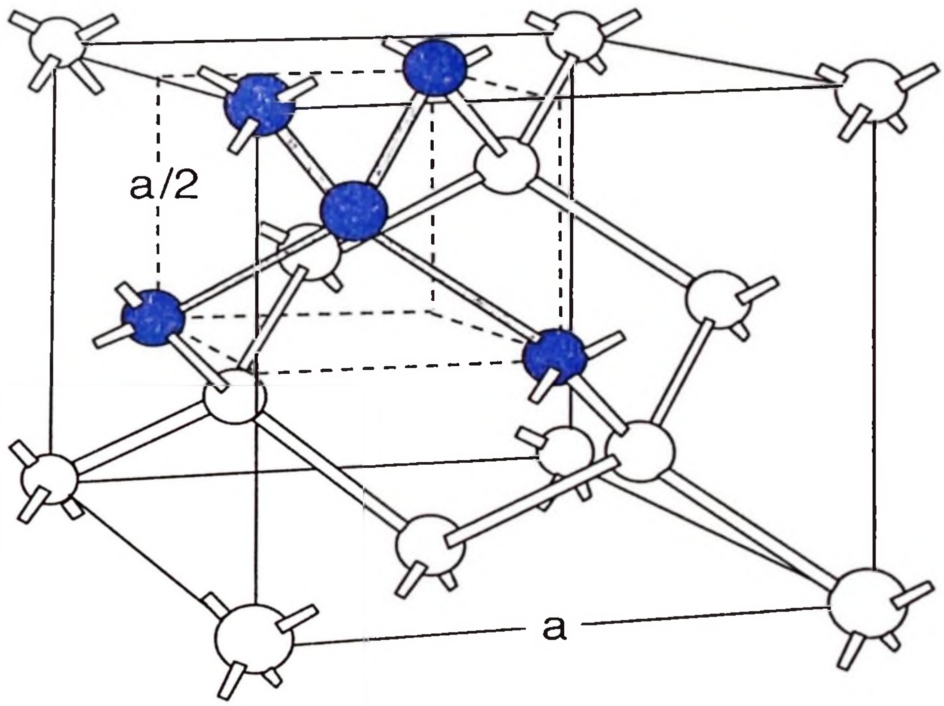

Figure 2.1: Si crystal with diamond lattice structure and defined lattice constant (a). Each atom is tetrahedrally bonded to four Si neighbors as displayed by dark atoms (El-Kareh, 2009).

Si has also a moderate band gap (E_g) of about 1.12 eV with a relatively high solid solubility of dopant atoms (Brillson, 1993, El-Kareh, 2009). Dopant atoms are the intentionally introduced atoms with different valence electrons which are used to fabricate n- and p-Si substrates with different electrical properties. For example, Si doped with nitrogen (with 5 valence electrons) would gain a net negative charge and Si doped with boron (with 3 valence electrons) would gain a net positive charge which is very important in fabrication of diodes and transistors. Moreover, the maturity of fabrication and processing techniques of device structures based on Si has made it the top choice for many electronic device applications (Brillson, 1993).

SiC, on the other hand, is a wide band gap semiconductor with $E_g > 2$ eV. SiC has a unique combination of electrical and thermo-physical properties which make it ideal semiconductor for preparation of devices operating at high temperatures, high power, and high frequencies. Figure 2.2 (a) and (b) demonstrates the atomic structure of SiC and hexagonal bilayer with alternating Si and C layers, respectively. Based on the stacking of Si and C layers numerous polytypes of SiC can be formed. The Most commonly applied and studied polytypes of SiC are the cubic 3C-SiC, and the hexagonal 4H-SiC and 6H-SiC, which are shown in Figure 2.2 (c-e), respectively. The interest in 4H–SiC for device fabrication has increased because of its higher electron mobility (800 cm^2/Vs) and wider band gap (3.26 eV) compared to that of 6H-SiC (400 cm^2/Vs and 3.03 eV) and 3C-4H-SiC (750 cm^2/Vs and 2.3 eV), respectively (Wijesundara and Azevedo, 2011). It now seems that most SiC-based electronic devices can be made on 4H-SiC with an improved performance, considering its superior advantages compared with other polytypes (Wijesundara and Azevedo, 2011).

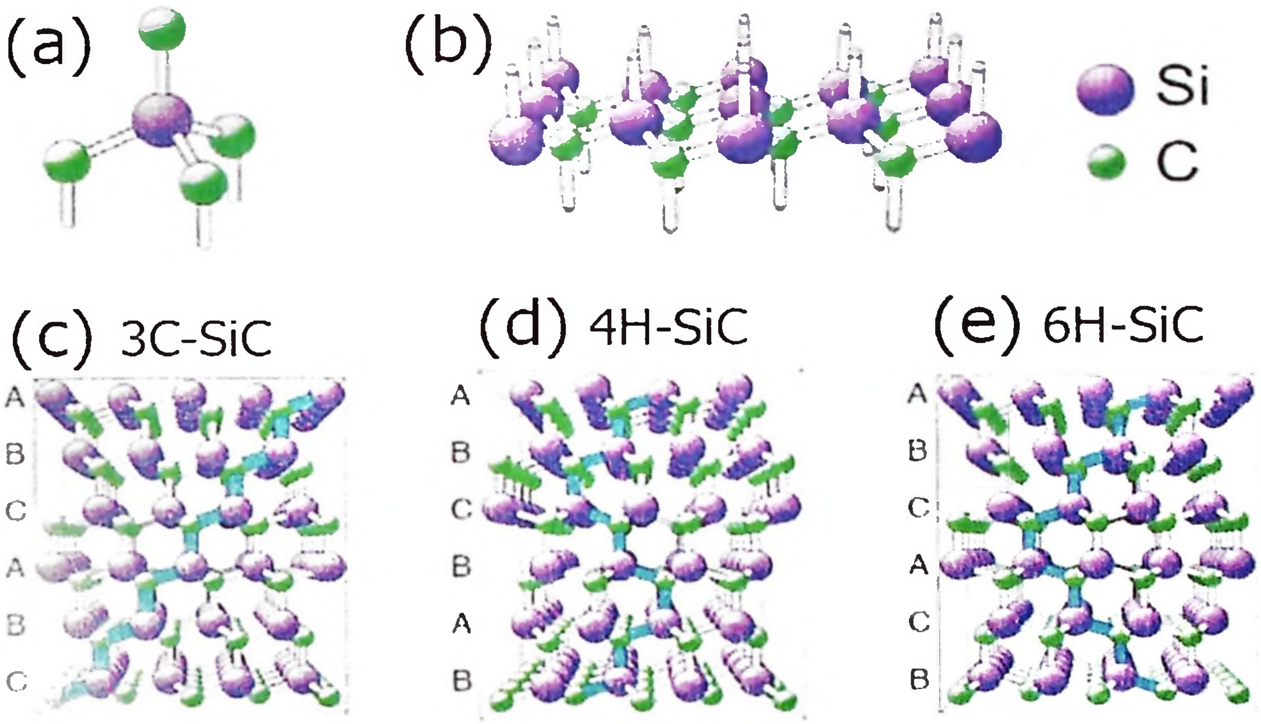

Figure 2.2: SiC atomic structure with tetrahedrally bonded Si-C cluster (a), and hexagonal bilayer with alternating Si and C layers (b). Most applicable polytypes of SiC include cubic 3C-SiC (a), hexagonal 4H-SiC (d) and 6H-SiC (e) (Wijesundara and Azevedo, 2011).

2.3 Nanoparticles Deposition Techniques

For deposition of the NPs on semiconductor surfaces, many techniques have been developed such as conventional lithography (Xia and Brueck, 2004), nanosphere lithography (Haynes and Van Duyne, 2001), nano-scale hole arrays filled with metals (Wen et al., 2012), ion-implantation (Ramaswamy et al., 2005), discontinuous thin film deposition (Olbrich et al., 1998), aerosol deposition (Hinds, 1982), anodic porous alumina nano-mask (Ruffino et al., 2010b), direct deposition self-assembly (Narayanan et al., 2000). The last four deposition techniques have been adopted as the first step of a two-step processing for fabrication of Schottky and Ohmic contacts with the second step being the contact metal deposition. Application of colloidal NPs, i.e. NPs dispersed and suspended in liquid solutions, is another way to deposit NPs on substrates by using different deposition techniques. This technique, however, has not been previously used for the fabrication of nanostructured contacts but has a great potential for such applications.

The semiconductor substrates on which NPs are deposited include Si (Narayanan et al., 2000), Ge (Kishore et al., 2012), SiC (Lee et al., 2002, Olbrich et al., 1997, Ruffino et al., 2010b, Kan et al., 2004, Kang et al., 2012a), GaN (Sohn et al., 2004a, Kim et al., 2006, Olbrich et al., 1997, Brown et al., 2000, Sohn et al., 2004b), $GaAs_{67}P_{33}$ (Olbrich et al., 1998), and InP (Bell and Kaiser, 1988). In this section each of these four methods, together with colloidal NPs deposition technique which was used and developed in this study, are briefly introduced and their advantages and disadvantages with respect to the final distribution of NPs and the reliability and adaptation to the final contact deposition step are briefly discussed and evaluated. Figure 2.3 depicts the processing steps and resulting NPs distributions of the four currently used NPs deposition techniques for nanostructured contact fabrication.

2.3.1 Discontinuous Thin Film Deposition

Deposition techniques such as thermal evaporation and sputtering are very common methods to create thin layers of metals on semiconductors. However, at the very early stages of deposition, when the nominal thickness of deposited thin film is usually less than 5 nm, the film is generally discontinuous and consists of arrays and islands of finite and yet very small-sized particles. The level of discontinuity and properties of a thin film and whether or not it has reached the percolation threshold is highly affected by the conditions of the applied deposition technique, temperature of the substrate and the chamber, and the vacuum level. These parameters would eventually contribute to the final shape and morphology of the resulted discontinuous films. The structure and temperature of the substrate and deposited atoms, and their interaction properties are among the most influential parameters (Malinský et al., 2012).

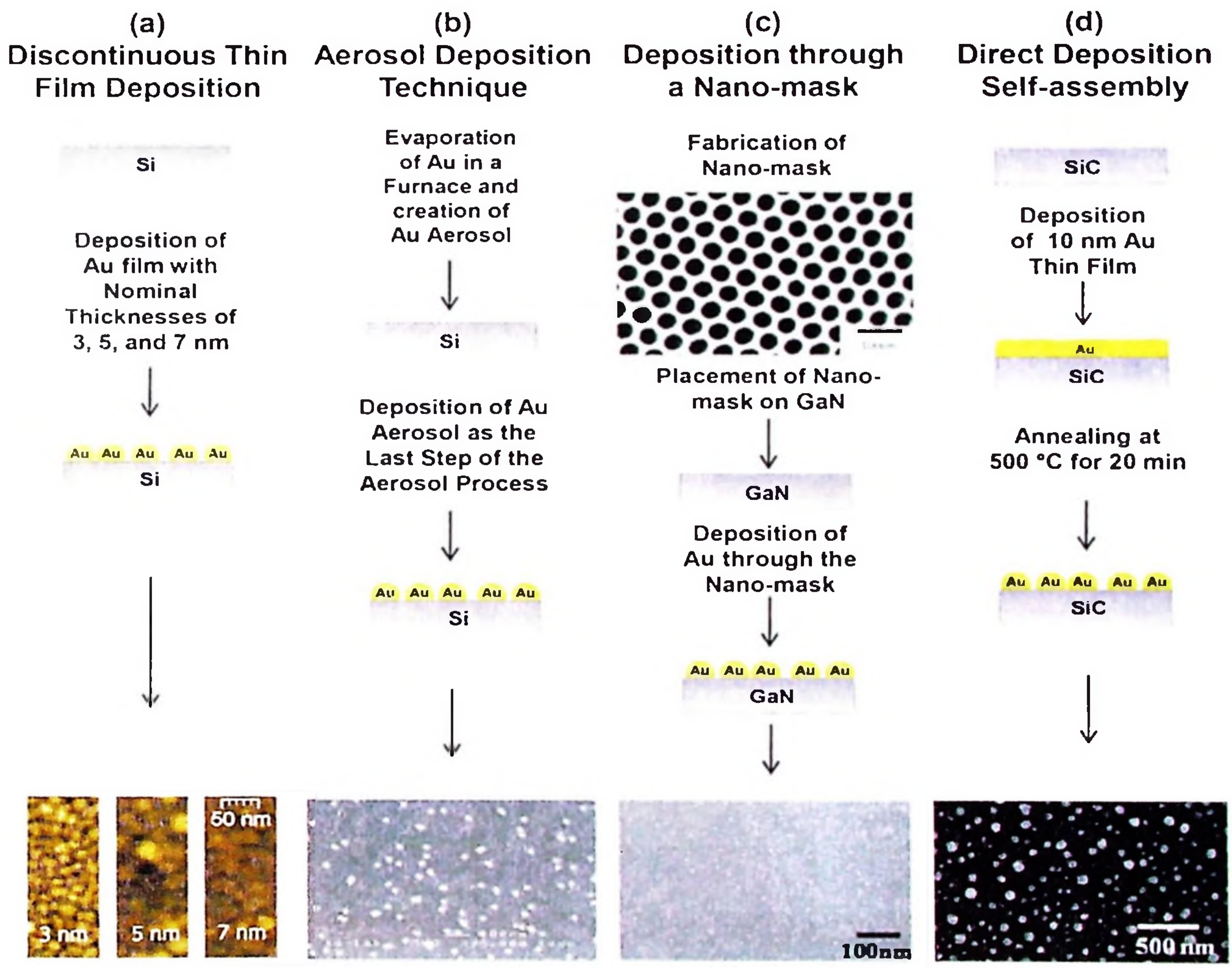

Figure 2.3: Schematic representation of required processing steps for deposition of Au NPs on different substrates and the corresponding SEM images of NPs distribution by using (a) discontinuous Au thin film deposition (Hövel et al., 2010), (b) aerosol method (Lee et al., 2002), (c) deposition through anodic porous alumina nano-mask (Sohn et al., 2004b), and (d) direct deposition self-assembly (Kang et al., 2012a).

Discontinuous metal thin films have been studied extensively under the subject of percolation threshold and transition from insulator to conductor behaviors. By deposition of metals with different nominal thicknesses to the threshold point where the clusters start to coalesce, the morphological and electrical properties of the discontinuous films can be controlled (Pal et al., 2004, Hövel et al., 2010). This method is perhaps the simplest technique with only one processing step for fabrication and deposition of NPs on any substrate. Another advantage is that the contact material can also be deposited immediately after NPs deposition without breaking the vacuum, depending on the capability and specifications of the machine used. On the other hand, despite the simple fabrication process, controlling and optimization of shape, size and uniform distribution of NPs can be quite challenging.

Olbrich et al. (1997 and 1998) directly deposited discontinuous nano-sized cobalt (Co) clusters on $GaAs_{67}P_{33}$ substrate by thermal evaporation. The effects of substrate temperature as well as altering the nominal thickness of deposited film on the final morphological properties of the nano-clusters were then comprehensively studied (Olbrich et al., 1998, Olbrich et al., 1997). Their results showed that the Co films with nominal thickness of 1 nm deposited on the substrates with 300 K temperature are already continuous, whereas the Co films on the substrate with 500 K were not continuous due the stronger coalescence of the impinging Co atoms in substrate high temperature. They also studied the effect of variable nominal thicknesses less than 1 nm (i.e. 0.25, 0.5, 0.8 nm) in both 300 K and 500 K substrate temperatures and correlated the morphological properties of the resulted Co discontinues film to the final electrical properties of the Schottky contacts. A typical representation of discontinuous thin film process and the resulting distribution of Au NPs are shown in Figure 2.3 (a).

2.3.2 Aerosol Deposition Technique

Aerosol deposition is based on vaporization and subsequent deposition of nano-sized particles on a substrate through a sequential processing step using tube furnaces, aerosol charger, and differential mobility analyzer (DMA). The material is first evaporated and aerosolized in a high-temperature tube furnace by heating to vapour pressure of the material. The aerosol particles are then being charged after passing through a photoelectric charging device. The charged particles are subsequently being size selected using a differential mobility analyzer (DMA). The DMA classifies the charged particles according to their mobility in an electric field. Since the aerosol particles leaving the furnace consist of agglomerates of small particles (3–5 nm in diameter), to make the particles compact and also to obtain spherical particles, they are reshaped in another furnace. The particle size is further controlled using a second similar DMA. The resulting aerosol particles are deposited onto the substrates in a deposition chamber where the NPs are precipitated using a perpendicular electric field. In order to avoid oxidation of the particles, the whole process is run under nitrogen carrier flow. The particle size and final density of NPs on the substrate can be manipulated by controlling the evaporation and reshaping temperature and also the deposition time. The aerosol generator setup and NPs production procedure are fully described by Magnusson et al. (1999).

Anand et al. (1996) and Lee et al (2002) (Figure 2.3 (b)) have used the same method to deposit Ag NPs (34 nm) and Au NPs (20 nm) on InP and SiC substrate, respectively and subsequently fabricated the nanostructured contacts. One of the main advantages of this technique is that the size and shape of NPs can be manipulated in a wide range. For example by changing the temperature of the furnaces or the DMA parameters, NPs with desired size, shape, and distribution can