Fabrication of nonlithographic semiconductor quantum wire infrared photodetector

Pavan Kumar Singaraju Venkata Sai

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FABRICATION OF NONLITHOGRAPHIC SEMICONDUCTOR QUANTUM WIRE

INFRARED PHOTODETECTOR

by

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Bachelor of Technology
Jawaharlal Nehru Technological University, India
2001

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science in Electrical Engineering
Department of Electrical and Computer Engineering
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ABSTRACT

Fabrication of Nonlithographic Semiconductor Quantum Wire Infrared Photodetector

by

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The thesis describes novel semiconductor quantum wire infrared photodetectors in the long- and very long-wavelength regions. The infrared photodetectors are based on intersubband transitions in semiconductor quantum wires and have the potential for higher operational temperature, increased signal-to-noise ratio, reduced dark current, wider spectral range and sensitivity to normal incident radiation. The quantum wire IR detectors were implemented using a nonlithographic nanostructure fabrication technique that is capable of producing large arrays of semiconductor quantum wires of a variety of materials and on different substrates. The operational principles, design procedure as well as the implementation of the quantum wire photodetectors using electrochemical anodization will be described.
TABLE OF CONTENTS

ABSTRACT ................................................................................................................................. iii

LIST OF FIGURES ...................................................................................................................... v

ACKNOWLEDGEMENTS ....................................................................................................... ix

CHAPTER 1 INTRODUCTION ................................................................................................ 1

CHAPTER 2 DEVICE DESIGN ................................................................................................. 5
  2.1 Device Structure & Operational Principle ................................................................. 5
  2.2 Mathematical Analysis ............................................................................................... 6
  2.3 Device Design ............................................................................................................. 10

CHAPTER 3 FABRICATION OF INFRARED DETECTORS ................................................. 15
  3.1 Anodization of aluminum .......................................................................................... 15
  3.2 Additive Technique (II-VI materials) ..................................................................... 20
  3.3 Subtractive Technique (III-V materials) ................................................................. 22

CHAPTER 4 EXPERIMENTAL PROCEDURE AND RESULTS ....................................... 26
  4.1 Anodization using 2% Sulfuric acid and 1% Citric acid ........................................... 27
  4.2 Anodization using 0.3M Oxalic acid and 1% Citric acid .......................................... 32
  4.3 Anodization in 10% Sulfuric acid and 1% Citric acid .............................................. 37

CHAPTER 5 CONCLUSION AND FUTURE WORK ......................................................... 40

REFERENCES ......................................................................................................................... 41

VITA ......................................................................................................................................... 44
LIST OF FIGURES

Figure 2-1 Schematic device structure of the quantum wire IR detector and its operational principle .............................................................................................................................................................................. 6

Figure 2-2 Energy levels of the GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As quantum wire material system as a function of diameter. E\textsubscript{1}, E\textsubscript{2} and E\textsubscript{2}-E\textsubscript{1} are the lowest two energy levels and intersubband transition energies for GaAs (active material). Thin lines: the lowest energy level for Al\textsubscript{x}Ga\textsubscript{1-x}As (the barrier material) as a function of diameter for different concentrations of x .............................................................................................................................................................................. 12

Figure 2-3 Quantum wire diameters and associated alloy concentrations for different detector cutoff wavelengths for the GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As material system ...................... 12

Figure 2-4 Energy levels of the GaN/Al\textsubscript{x}Ga\textsubscript{1-x}N quantum wire material system as a function of diameter. E\textsubscript{1}, E\textsubscript{2} and E\textsubscript{2}-E\textsubscript{1} are the lowest two energy levels and intersubband transition energies for GaN (active material). Thin lines: the lowest energy level for Al\textsubscript{x}Ga\textsubscript{1-x}N (the barrier material) as a function of diameter for different concentrations of x .............................................................................................................................................................................. 13

Figure 2-5 Quantum wire diameters and associated alloy concentrations for different detector cut off wavelengths for the GaN/Al\textsubscript{x}Ga\textsubscript{1-x}N material system ...................... 13

Figure 2-6 Energy levels of the CdTe/Zn\textsubscript{x}Cd\textsubscript{1-x}Te quantum wire material system as a function of diameter. E\textsubscript{1}, E\textsubscript{2} and E\textsubscript{2}-E\textsubscript{1} are the lowest two energy levels and intersubband transition energies for CdTe (active material). Thin lines: the lowest energy level for Zn\textsubscript{x}Cd\textsubscript{1-x}Te (the barrier material) as a function of diameter for different concentrations of x .............................................................................................................................................................................. 14
energy level for ZnxCd1-xTe (the barrier material) as a function of diameter for different concentrations of x

Figure 2-7 Quantum wire diameters and associated alloy concentrations for different detector cut off wavelengths for the CdTe/ZnxCd1-xTe material system

Figure 3-1 Schematic top and cross sectional views of the hexagonal arrays of pores formed in porous alumina template

Figure 3-2 Voltage Time characteristics during anodization of bulk aluminum

Figure 3-3 Voltage Time characteristics during anodization of thin aluminum film on Silicon Substrate

Figure 3-4 Schematic cross sections of quantum wire IR detectors implemented by the a) additive and b) subtractive techniques

Figure 3-5 Scanning Electron Microscope image of a thin film porous alumina template formed by the two step anodization process

Figure 3-6 The schemes of pillar growth and pits formation in the pillars center

Figure 3-7 Schematic diagram showing the subtractive technique for the fabrication of semiconductor quantum wire IR photodetectors

Figure 4-1 Voltage time relationship obtained during anodization in 2% sulfuric acid at a current density of 40 mA/cm²

Figure 4-2 Cross sectional view of the Al/Ta bilayer anodized in sulfuric acid at a current density of 40mA/cm²

Figure 4-3 Cross sectional view of the Al/Ta bilayer anodized in sulfuric acid at 40mA/cm² showing the initiation of Ta₂O₅
Figure 4- 4 Voltage time relationship obtained using 1% citric acid at a current density of 0.5 mA/cm² @ 1°C ................................................................. 30

Figure 4- 5 Top view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm² ................................................................. 30

Figure 4- 6 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm² ....................................................... 31

Figure 4- 7 Top view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 1.5mA/cm² ................................................................. 31

Figure 4- 8 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 1.5mA/cm² ....................................................... 32

Figure 4- 9 Voltage time relationship obtained using 0.3M Oxalic acid with a current density of 40mA/cm² ................................................................. 33

Figure 4- 10 Top view of the sample anodized in 0.3M oxalic acid at a current density of 40mA/cm² ................................................................. 34

Figure 4- 11 Cross sectional view of the Al/Ta Bilayer anodized in 0.3M Oxalic acid at a current density of 40mA/cm² ................................................................. 34

Figure 4- 12 Voltage time relationship obtained using 1% citric acid at a current density of 0.5 mA/cm² @ 1°C ................................................................. 35

Figure 4- 13 Top view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm² ................................................................. 36

Figure 4- 14 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm² ................................................................. 36
Figure 4-15 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm$^2$ .............................................................. 37

Figure 4-16 Voltage Time Characteristics obtained during constant current anodization done in 10% sulfuric acid @19°C ................................................................. 38

Figure 4-17 Voltage Time Characteristics obtained during constant current anodization done in 1% citric acid @19°C ................................................................. 38

Figure 4-18 Top view of the tantalum oxide pillars on Silicon Substrate .................... 39

Figure 4-19 Cross section of the Tantalum oxide pillars on Silicon substrate ............... 39
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CHAPTER 1

INTRODUCTION

Infrared (IR) photodetectors operating in the medium wavelength IR (MWIR: 3-5 \(\mu\)m), long wavelength IR (LWIR: 8-12 \(\mu\)m), and very long wavelength IR (VLWIR: > 12 \(\mu\)m) regions are important for many civilian and military applications [1]-[3]. Traditionally, cooled material systems such as indium antimonide, platinum silicide, mercury cadmium telluride, and arsenic doped silicon (Si:As) have been the primary IR detection technologies. However, the use of intersubband optical absorption in low dimensional semiconductors has emerged as a promising technique for IR detection. In particular, Quantum Well Infrared Photodetectors (QWIP) have been the topic of significant research and development during the past decade [4]-[6], and QWIP detectors for mid- and long-wavelength IR have been successfully implemented [7]-[9] using primarily GaAs, InGaAs, and SiGe [10]. Due to this effort, QWIP devices have emerged as an alternative technology for the implementation of high performance Focal Plane Array (FPA) detectors that show enhanced performance compared to bulk material detectors such as HgCdTe and InSb [1],[5]. While this is a very promising technology, QWIPs have several important limitations as described below. (i) For the predominantly n-type QWIPs, optical absorption is limited to radiation with an electric field component
along the growth axis, thus prohibiting the detection of normal incident infrared light [11]. This drawback is typically overcome by using diffraction gratings, prisms or a slope edge profile of pixels, adding to the fabrication and structural complexity. (ii) The IR response range for QWIPs is relatively narrow. (iii) Most QWIP devices are fabricated on GaAs or InP substrates, whereas the readout and integration circuitry are silicon based. As a result, hybrid bonding techniques are required to couple the QWIPs with silicon circuitry [12].

To address the limitations of QWIP detectors, there has been significant interest in IR detectors with lower dimensions such as quantum wires (1D) and quantum dots (0D) [13]-[17]. The use of quantum wires and quantum dots for IR detection provides many advantages as summarized below. (a) The confinement of carriers in 1D and 0D nanostructures allow the absorption of normally incident IR radiation, thus eliminating the need for external gratings or the need for angular incidence. (b) The discrete bound energy states in 1D and 0D structures give rise to increased carrier capture and relaxation time due to reduced phonon scattering [18]-[19]. The increased capture and relaxation times allow enhanced carrier extraction efficiency thus increasing the detector signal-to-noise ratio. In addition, since the photodetector detectivity is proportional to the square root of the carrier capture time [20], 1D and 0D detectors have the potential for higher temperature operation. (c) The repressed phonon scattering in 1D and 0D detectors is also expected to significantly reduce the detector dark current [21]-[22]. (d) The intersubband spacing in quantum wires and dots can be controlled by controlling the dimensions, and thus the peak detector responsivity can be tuned to the desired IR wavelength by
changing the device dimension. This is unlike QWIP detectors, where the energy separation can be altered only by varying the alloy concentration.

The advantages of 1D and 0D IR detectors have led to a strong interest in this area, and a number of IR detectors based on quantum dots have been demonstrated [13]-[17]. However, most of these are implemented using the Stransky-Krastanov growth mode, which restricts both the quantum dot material and the size, and hence the IR cutoff wavelength. The UNLV nanotechnology research group has developed a low cost nonlithographic nanostructure fabrication technique that is particularly appropriate for the implementation of quantum wire IR detectors over a wide spectral range []. This technique is based on the nonlithographic fabrication of semiconductor quantum wire arrays through the use of a pre-formed thin film template of nanoporous alumina. This technique provides flexibility in the choice of nanostructure composition, length, diameter, and dimensionality (i.e. quantum wire or dot). This approach has the additional advantages that: (i) hexagonal ordering of the quantum wires is expected to improve signal to noise ratio by averaging out random noise, (ii) the high packing density provide many quantum wires in each pixel thus improving device redundancy, and (iii) this technique allows the fabrication of the IR detectors on silicon substrates, which provide higher mechanical strength, the availability of large area substrates, and more straightforward integration with silicon electronics.

The objective of this thesis was to develop the process technology for the fabrication of quantum wire infrared detectors on silicon substrates. The rest of the thesis is organized as follows. Chapter 2 discusses operational principle, mathematical analysis
and design of the infrared detectors. Chapter 3 explains the two fabrication techniques for the Infrared detectors. Chapter 4 explains the experimental procedure and results. Chapter 5 gives the conclusions from the thesis and the suggested future work.
CHAPTER 2

DEVICE DESIGN

2.1 Device Structure & Operational Principle

A schematic structure of the quantum wire infrared photodetector proposed by our group is shown in Figure 2.1 [35]. The device contains a junction formed by a quantum wire active layer and a quantum wire barrier layer, both of which terminate in ohmic contacts. The IR radiation incident near the junction generates photocarriers, which are collected by the application of a bias voltage between the ohmic contacts. The device operation can be understood from the energy band diagrams in the current flow direction (y-axis) and carrier confinement directions (x- and z- axes) shown in Figure 2.1. The ground state of the barrier layer quantum wire (with a higher band-gap) is at a slightly higher level than the first excited state ($E_2$) of the active layer quantum wire. In the absence of IR radiation, only the lowest sub-band $E_1$ of the active layer quantum wire is populated with electrons, which do not have sufficient energy to overcome the potential barrier across the junction. The absorption of IR energy moves some of the electrons from $E_1$ to the next higher sub-band level $E_2$; these higher energy electrons can now easily cross into the barrier layer, thus giving rise to a photocurrent.
2.2 Mathematical Analysis

The values of various energy levels in a quantum wire with a circular cross section are calculated as follows. The Schrödinger wave equation in cylindrical polar coordinates for such a structure is given by

\[
-\frac{\hbar^2}{2m_{\text{eff}}} \nabla^2 + V(r) \psi(r,\theta, y) = E\psi(r,\theta, y)
\]

where \( m_{\text{eff}} \) is the effective mass of the electron, \( V(r) \) is the confinement potential of the quantum wire and \( E \) is the eigen energy.

Separating the circular and the linear parts

\[
\psi(r,\theta, y) = C(r,\theta)\psi(y)
\]

gives, with the (arbitrary) choice \(-E_y\) as the separation constant

\[
\frac{\hbar^2}{2m_{\text{eff}}} \frac{1}{C(r,\theta)} \frac{\partial^2}{\partial y^2} C(r,\theta) + V(r) - E \psi(y) = \frac{\hbar^2}{2m_{\text{eff}}} \frac{1}{\psi(y)} \frac{\partial^2 \psi(y)}{\partial y^2} = -E_y
\]

so we can define the simple \( y \) solutions as
and because the crystal is presumed periodic in \( y \), we obtain allowed values of \( k \) that are spaced by \( 2\pi/L_y \).

For the remaining "circular" part, we note that

\[
\nabla_{r\theta}^2 = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{r \partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2}
\]

Hence, we have

\[
\left[ \frac{\hbar^2}{2m_{\text{eff}}} \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{r \partial}{\partial r} \right) + \frac{\hbar^2}{2m_{\text{eff}}} \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + V(r) \right] C(r, \theta) = E_{r\theta} C(r, \theta)
\]

where \( E_{r\theta} = E - E_y \)

Now we can postulate a form

\[ C(r, \theta) = R(r)A(\theta) \]

which leads to

\[
-\frac{\hbar^2}{2m_{\text{eff}}} \frac{A(\theta) r \partial}{r \partial r} R(r) + V(r)R(r)A(\theta) - \frac{\hbar^2}{2m_{\text{eff}}} \frac{R(r) \partial^2 A(\theta)}{r^2 \partial \theta^2} = E_{r\theta} R(r)A(\theta)
\]

Dividing by

\[
-\frac{\hbar^2}{2m_{\text{eff}}} \frac{R(r)A(\theta)}{r^2}
\]

and choosing \( B \) as the separation constant, we get

\[
\frac{r}{R(r)} \frac{\partial}{\partial r} \left( \frac{2m_{\text{eff}}}{\hbar^2} r^2 V(r) + \frac{2m_{\text{eff}}}{\hbar^2} r^2 E_{r\theta} \right) = -\frac{1}{A(\theta)} \frac{\partial^2}{\partial \theta^2} = B
\]

Hence we have
\[ \frac{\partial^2 A}{\partial \theta^2} = -BA \]

\[ A = e^{im\theta} \quad \text{(or formally \quad } Ee^{im\theta} + Fe^{-im\theta}) \]

with \[ B = m^2 \]

where \( m \) is taken as an integer so that for each complete cycle the wave function returns to the same value.

For the equation, we now have

\[ r \frac{\partial}{\partial r} \left( r \frac{\partial R}{\partial r} \right) - r^2 \frac{2m_{\text{eff}}}{\hbar^2} \left[ V(r) - E_{r_0} \right] R = m^2 R \]

Assuming an infinite potential (which is the case for these quantum wires), \( V(r) = 0 \) within the cylinder and \( V(r) = \infty \) outside the cylinder. The " \( V(r) = \infty \) at \( r = r_0 \)" condition forces the boundary condition \( R(r_0) = 0 \), and we get the equation

\[ r \frac{\partial}{\partial r} \left( r \frac{\partial R}{\partial r} \right) + \left[ r^2 \varepsilon - m^2 \right] R = 0 \]

where

\[ \varepsilon = \frac{2m_{\text{eff}}}{\hbar^2} E_{r_0} \]

or equivalently

\[ \frac{\partial}{\partial r} \left( r \frac{\partial R}{\partial r} \right) + \left[ r^2 \varepsilon - m^2 \right] R = 0 \]

The solution of this equation is, from standard mathematical reference books

\[ R(r) = DJ_p(\sqrt{\varepsilon}r) + GY_p\sqrt{\varepsilon}r \]
where D and G are arbitrary constants and Jp and Yp are, the Bessel and the Weber functions respectively of order p.

The Weber functions diverge as \( r \to 0 \), which would necessarily lead to a wave function \( C(r, \theta) \) that is infinite or discontinuous through \( r=0 \) for atleast some angles, which would be unphysical, so we discard the Weber functions. Thus we have

\[
R(r) \propto J_m \sqrt{(er)}
\]

From mathematical reference books on Bessel functions,

\[
J_{-m}(x) = (-1)^m J_m(x)
\]

Since the sign of the wave function is an arbitrary choice for eigen value problems, we can therefore write,

\[
R(r) \propto J_{|m|} \sqrt{(er)}
\]

For eigen function solutions, we have to meet the boundary condition \( R(r_o)=0 \). Hence we require

\[
J_{|m|} \sqrt{(er)} = 0
\]

Writing the nth zero of the mth order Bessel Function as \( s_{nm} \), we therefore have

\[
\sqrt{\varepsilon_{nm}} r_o = s_{nm}
\]

i.e.,

\[
\varepsilon_{nm} = \frac{s_{nm}^2}{r_o^2}
\]

or

\[
E_{nm} = \frac{\hbar^2}{2m_{eff} r_o^2} s_{nm}^2
\]
where \( m \) is any positive or negative integer or zero, and \( n \) is any positive integer > 0.

2.3 Device Design

The quantum wire IR detectors can be implemented using a variety of group III-V, group IV and group II-VI semiconductors. The device design involves the identification of the active and the barrier layer materials and the quantum wire dimensions. Examples of II-VI semiconductor materials that can be used as active and barrier layers include CdSe, CdS, CdTe and their alloys such as CdSSe, CdZnSe, etc. Similarly, examples of III-V semiconductor materials include GaAs, GaN, InGaAs and their alloys such as AlGaAs, AlGaN and InGaN. We have selected three different material systems (due to their suitability for IR detection) to demonstrate the design procedure of the quantum wire detectors.

Figure 2.2 shows the lowest two energy levels (\( E_1 \) and \( E_2 \)) and the intersubband transition energies (\( E_2-E_1 \)) for GaAs quantum wires (active layer) for different dimensions. Figure 2.2 also shows the lowest energy levels for Al\(_x\)Ga\(_{1-x}\)As quantum wires (barrier layer) as a function of diameter for different alloy concentration \( x \). The energy levels were calculated from the zeros of the Bessel functions as discussed in the previous section. The material and heterojunction parameters were obtained from published literature [23] – [26]. The reference energy level selected is the bulk conduction band energy of the active quantum wire material (GaAs in Figure 2.2). The effects of conduction band discontinuities at the heterojunctions as well as the dependence of effective mass on alloy concentrations were properly taken into account for energy calculations. In Figure 2.2 we have selected the IR absorption wavelength of \(~20 \mu\text{m}\).
(~62 meV) to demonstrate the design procedure; this is indicated by the horizontal line in Figure 2.2. This particular wavelength has important military applications. From Figure 2.2, the quantum wire diameter needed for intersubband absorption energy of 62 meV is approximately 18 nm. Since the barrier layer quantum wire (Al\textsubscript{x}Ga\textsubscript{1-x}As) has the same diameter as the active layer quantum wire (GaAs), the alloy concentration x of the barrier layer material needs to be determined for proper device operation. For room temperature operation of the IR detectors, it is necessary that the lowest energy level of the barrier layer quantum wire be at least 26 meV above the lowest energy level E\textsubscript{1} of the active layer quantum wire. In addition, the lowest energy level of the barrier layer quantum wire should be close to the first excited state of the active layer quantum wire (E\textsubscript{2}). In Figure 2.2, the vertical line (at 18 nm diameter) intersects with E\textsubscript{2} and the Al\textsubscript{x}Ga\textsubscript{1-x}As energy level for an alloy concentration of x=0.06, which should be selected for proper device operation. Thus a quantum wire diameter of 18 nm is required with an alloy concentration x=0.06 for a GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As quantum wire IR photodetector to operate at 20 μm. For other IR wavelengths, a similar design procedure can be followed to determine the device parameters. Figure 2.3 shows the quantum wire diameter and the associated alloy concentration for IR detectors at different cutoff wavelengths for the GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As material system. Figures 2.4-2.7 show similar results for GaN/Al\textsubscript{x}Ga\textsubscript{1-x}N and CdTe/Zn\textsubscript{x}Cd\textsubscript{1-x}Te material systems.
Figure 2-2 Energy levels of the GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As quantum wire material system as a function of diameter. E\textsubscript{1}, E\textsubscript{2} and E\textsubscript{2} - E\textsubscript{1} are the lowest two energy levels and intersubband transition energies for GaAs (active material). Thin lines: the lowest energy level for Al\textsubscript{x}Ga\textsubscript{1-x}As (the barrier material) as a function of diameter for different concentrations of x.

Figure 2-3 Quantum wire diameters and associated alloy concentrations for different detector cutoff wavelengths for the GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As material system.
Figure 2-4 Energy levels of the GaN/AlxGa1-xN quantum wire material system as a function of diameter. E1, E2 and E2-E1 are the lowest two energy levels and intersubband transition energies for GaN (active material). Thin lines: the lowest energy level for AlxGa1-xN (the barrier material) as a function of diameter for different concentrations of x.

Figure 2-5 Quantum wire diameters and associated alloy concentrations for different detector cut off wavelengths for the GaN/AlxGa1-xN material system.
Figure 2-6 Energy levels of the CdTe/ZnxCd1-xTe quantum wire material system as a function of diameter. E1, E2 and E2-E1 are the lowest two energy levels and intersubband transition energies for CdTe (active material). Thin lines: the lowest energy level for ZnxCd1-xTe (the barrier material) as a function of diameter for different concentrations of x.

Figure 2-7 Quantum wire diameters and associated alloy concentrations for different detector cut off wavelengths for the CdTe/ZnxCd1-xTe material system.
CHAPTER 3

FABRICATION OF INFRARED DETECTORS

The essential component of the proposed infrared detector is a quantum wire heterostructure of dimension in the range of 10-20 nm. It will be necessary to have a large number of quantum wires in parallel in order to get reasonable signal strength. Such structures are difficult, and often impossible, to implement using standard electron beam lithography and etching techniques. Nonlithographic self assembled techniques, which capitalize on natural self organization, are more appropriate for the implementation of such quantum wire arrays. The Nanotechnology Research Group at UNLV has developed a nonlithographic nanofabrication technique that is particularly appropriate for the implementation of the quantum wire infrared detectors. The technique is based on the use of a thin film anodized alumina, formed by anodization that is used as a guide for the fabrication of the nanostructures.

3.1 Anodization of aluminum

When aluminum is exposed to atmosphere it forms a very thin layer of oxide (alumina) that adheres strongly to the surface and protects it from further reaction. A thick layer of oxide can be formed by immersing aluminum in an electrolytic solution and passing electric current; this process of oxidizing aluminum electrochemically is called anodization. The anodized aluminum contains a two dimensional hexagonal lacework of cells with
uniform tubular pores. The schematic of the top and the cross section of the porous alumina are shown in fig 3.1. The diameter of the pores and the thickness of the alumina depend on the conditions of anodization such as type and pH of the electrolytic solution, anodizing current density and time. The diameter of the pores can vary from 4nm to 200 nm, pore length from 10nm to 1000's of nm. Also, the density of these pores can range from $10^9$ to $10^{11}$ cm$^{-2}$ range. Although the process of anodization has been around for years, the mechanism of pore formation is not fully understood yet. A near perfect, densely packed self organized hexagonal pore structures for a narrow processing parameters have been reported by researchers in the last 20 years. The cause of this self ordering behavior is believed to be mechanical stress which leads to repulsive interaction between neighboring pores as reported by Jessensky et al [31].

![Figure 3-1 Schematic top and cross sectional views of the hexagonal arrays of pores formed in porous alumina template](image)

The process of anodization can be carried out using two different conditions, by applying constant current or by applying constant voltage. An explanation for the various
stages during constant current anodization is given here because majority of the experiments in this thesis were carried out using this condition. The easiest way to monitor the anodization process is to measure the voltage time characteristics. A typical curve during the anodization of bulk aluminum is shown in fig 3.2. A thin layer of nonporous alumina \((\text{Al}_2\text{O}_3)\) is formed during the first 3-5 sec. This is represented by an increase in the voltage that corresponds to an increase in the net resistance. As the process of anodization is continued, an array of pores develops on the surface and they grow in diameter before reaching the final dimension that is determined by the processing conditions. This is indicated by the decrease in the potential that is measured. The potential finally reaches a steady state value when the final diameter is reached. The diameter of the pores does not increase any further after this and the depth of the pores increases with continuing anodization. Over the years, anodization of bulk aluminum has been investigated quite extensively; however such structures are not suitable for practical device applications because of the thick unreacted bulk aluminum underneath. To overcome this limitation, the Nanostructures Research Group has developed the technology for creating a thin film alumina template on an arbitrary substrate.

The Voltage-Time characteristic during constant current anodization of an aluminum film deposited on a silicon substrate is shown in fig 3.3. As seen from the figure, the voltage increases rapidly during the first 3-5 sec due to the formation of a nonporous (dense) alumina layer. The voltage then decreases and reaches a steady state value marked by the formation of pores and reaching the final diameter. After this, the pores grow in a direction perpendicular to the surface of the substrate. When the pores reach the silicon surface the voltage level again increases, which is believed to be due to the oxidation of the
silicon substrate. The pore formation rate can be accurately modeled because the thickness of the film is known and also the total time for anodization can be obtained from the voltage time characteristics. As a result, this approach not only gives the control on the pore diameters but also on the depth of the pores.

**Pore Formation on Bulk Aluminum**

![Diagram](image)

Figure 3-2 Voltage Time characteristics during anodization of bulk aluminum

**Pore Formation on Thin Aluminum**

![Diagram](image)

Figure 3-3 Voltage Time characteristics during anodization of thin aluminum film on Silicon Substrate
The periodicity of the pores can be improved by using a two step anodization process. The anodization in the first step is done using a constant voltage method where the aluminum film is anodized to approximately one-third of its thickness. The anodization by constant voltage gives good periodicity of the pores. The alumina film is then etched using a mixture of chromic acid solution and phosphoric acid. This completely removes the alumina layer and leaves behind foot-prints on the aluminum film. The next step of anodization is carried out using constant current; the pores tend to grow only in the areas of already existing foot-prints. The applied current density controls the diameter of the pores. Thus good control on the periodicity and the pore diameter can be obtained by using this technique.

The template based fabrication technique can be either (i) additive, where the semiconductor material can be grown into wires guided by the template, or (ii) subtractive, where the semiconductor quantum wires are formed by the guided etching of a 2D material system guided by the template. Figure 3.4 shows schematic cross-sections of the IR detectors that can be formed by the additive and the subtractive techniques. The two methods are described in the following sections.

![Figure 3.4 Schematic cross sections of quantum wire IR detectors implemented by the (a) additive and the (b) subtractive techniques](image-url)

Figure 3-4 Schematic cross sections of quantum wire IR detectors implemented by the a) additive and the b) subtractive techniques
3.2 Additive Technique (II-VI materials)

This technique is particularly suitable for quantum wires of II-VI compound semiconductors, for which the electrochemical synthesis techniques are well developed. In this method, the quantum wires are formed by electrochemical deposition of the specific semiconductor materials inside the template pores. A typical fabrication procedure is as follows.

As an example of implementing quantum wire IR detectors on silicon substrates, p-type <100> 0.1-0.3 ohm-cm silicon wafers are first cleaned using a standard technique and etched in a 1% hydrofluoric acid solution to remove any native oxide. Next, a 0.5 μm thick aluminum layer is deposited on the back of the wafers and annealed at 450° C for 30 minutes to form a good electrical contact. Following this, a thin layer of platinum is deposited on the top surface of the wafer to prevent anodic oxidation of the silicon surface and to assist in alumina barrier layer removal. Next, a pure (99.999%) aluminum layer approximately 0.5 μm thick is deposited by electron beam evaporation and annealed at 400° C for 30 minutes to ensure good adhesion. The top aluminum layer is then anodized in 10% sulfuric or 0.3M oxalic acid under constant voltage or constant current conditions. Anodization in sulfuric acid creates templates with smaller pore diameters compared to anodization in oxalic acid under similar conditions. Constant current anodizations are performed at current densities ranging between 10 and 70 mA/cm², and constant voltage anodizations are typically carried out at voltages ranging between 10 and 40 Volts. The acid solution is circulated using a pump and chilled using a chiller to prevent heat buildup at the aluminum/electrolyte interface. The anodization process is monitored by observing the voltage-time (for constant current anodizations) or current-
time (for constant voltage anodizations) characteristics. As mentioned before, a two-step anodization process is used to improve pore size uniformity and pore periodicity. In this process, first around 0.25 micron of aluminum is anodized and the resulting porous alumina is completely removed using a chromic acid etch. The remaining aluminum layer is then anodized again until the pores reach the platinum surface. Figure 3.5 shows the field emission scanning electron microscope image of an alumina template formed on silicon substrates by the two-step anodization process.

![Scanning Electron Microscope image of a thin film porous alumina template formed by the two step anodization process](image)

To form the quantum wires, II-VI binary and ternary semiconductor materials are synthesized inside the pores through direct-current, underpotential deposition in a non-aqueous solution. The use of underpotential deposition (~1 nm/min) provides near atomic-layer control over the deposition process enabling the formation of abrupt heterojunctions required for the photodetectors. After the active layer (e.g., CdSe) is synthesized to the desired length, the growth process is paused by stopping the applied
current. Then, without removing the device from the electrochemical bath, the alloying material (e.g. S) is added to the solution. When the electrochemical solution reaches a steady state, material growth is continued by applying the appropriate current to form the barrier quantum wire. The barrier layer formation is continued to form a thin continuous layer on top of the template to enable the formation of ohmic contacts. For II-VI materials, the top ohmic contact can be formed by the deposition of Aluminum through a shadow mask onto the thin layer of bulk semiconductor followed by an annealing step. The platinum layer on top of the silicon surface forms the second contact. However, alternative materials (e.g., Cu, Au, Al) may be used to enhance device performance. Since IR photons are not energetic enough to create electron-hole pairs, it is necessary to populate the conduction band of the active quantum wire with electrons. Most II-VI materials are n-type as-grown, however, dopants can be added to the electrochemical solution (e.g., Cu and Te for CdSe) to more precisely control the electron density. Doping of II-VI materials during electrochemical synthesis is a well-established technique that is extensively used for photovoltaic applications.

3.3 Subtractive Technique (III-V materials)

This technique is particularly appropriate for III-V compound semiconductors, which are difficult to synthesize electrochemically. In this case, the starting material will be a thin film heterostructure of the active and barrier materials (such as GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As heterostructure) from which the quantum wires would be formed using a template guided etching technique. An inverse pattern transfer technique is used to form the quantum wires as shown in the process flow diagram in Figure 3.7. In this technique, a thin layer
of tantalum (~40 nm) is first deposited on the heterostructure surface followed by the deposition of a layer of aluminum (~500 nm). Next, the aluminum film is anodized to form an alumina template using the substrate as the back contact. The two-step anodization process, as outlined in the previous chapter, can be used to improve pore uniformity and periodicity. The Ta layer also acts as a protective barrier between the anodizing electrolyte and the semiconductor thin film underneath. The Ta layer is then oxidized by anodization in citric acid; in this process the tantalum oxide (Ta$_2$O$_5$) grows inside the pores, with some spreading underneath. The growth of Ta$_2$O$_5$ inside the pores of an alumina template has been demonstrated by Vorobyova [34]. The porous alumina layer is then removed by etching in a phosphoric/chromic acid solution to form free-standing tantalum oxide pillars.

A schematic representation of the pillar growth is presented in fig 3.7 to give a clear understanding of the process. This process can be divided into two different stages. During the first stage, anodization of aluminum occurs. Once reaching the Al/Ta interface the anodization of Ta film begins only because of the migration of oxygen ions and the oxidation of residual Al ions continues. In the second stage, when the anodization is performed in 1% citric acid, the pores are filled with the tantalum oxide. This does not happen until the Al$_2$O$_3$ barrier layer is completely dissolved. After the full dissolution of alumina the tantalum oxide pillars grow inside the pores.

The pillar structures are then transferred to the substrate material using Reactive Ion Etching (RIE), thus forming the desired quantum wires. To expose the heterostructure surface around the pillars, the Ta$_2$O$_5$ thin film (and any un-oxidized Ta layer) is first etched using RIE. The etching characteristics of tantalum and tantalum oxide have both...
been investigated during the last decade due to the application of these materials in active matrix liquid crystal displays (AMLCDs), DRAMS, and as an alternative dielectric material for advanced CMOS devices. It has been observed that the plasma etch properties of tantalum and tantalum oxide are qualitatively similar to that of silicon and silicon dioxide. As a result, a selective etch for either material can be obtained by using CF$_4$ (Ta$_2$O$_5$) or CHF$_3$ (Ta), with a typical etch selectivity in either case of approximately 10:1. The quantum wires are then formed by RIE etching of the semiconductor surface using the Ta$_2$O$_5$ pillars as etch masks. As one example, for the case of silicon, an SF$_6$ based etch chemistry can be used to anisotropically etch silicon with good etch selectivity to the tantalum oxide (10:1). For GaAs/AlGaAs heterostructures, the use of BCl$_3$/Cl$_2$ etch chemistries have been demonstrated to form quantum wires with good side-wall profiles and little material damage. The Ta$_2$O$_5$ pillars are then removed which is followed by the formation of ohmic contacts.

Figure 3-6 Schematic diagram showing the subtractive technique for the fabrication of semiconductor quantum wire IR photodetectors.
Figure 3-7 The schemes of pillar growth and pits formation in the pillars center

a) Al porous anodization
b) Reaching the Al-Ta interface by the anodization front
c) Formation of Ta$_2$O$_5$ oxide with simultaneous Al$_2$O$_3$ electrochemical dissolution
d) Chemical dissolution of pore walls during exposure in the anodizing electrolyte
e) The moment of full Al$_2$O$_3$ dissolution and Ta$_2$O$_5$ pore filling start
f) Ta$_2$O$_5$ formation at the barrier layer/metal interface and the oxide/electrolyte interface
CHAPTER 4

EXPERIMENTAL PROCEDURE AND RESULTS

Anodization of aluminum can be carried out in different electrolyte solutions like sulfuric acid, oxalic acid, phosphoric acid etc., the pH of the electrolyte along with the mode of anodization, constant current or constant voltage, determines the size and periodicity of the pores. In a typical fabrication procedure, a tantalum film of thickness 200nm is first deposited on a p-Si wafer. Next an aluminum layer of thickness 500nm is deposited on top of the tantalum film. The metal depositions in this project were carried out in the Nanotechnology Center at University of California, Santa Barbara. The Al/Ta coated wafer was then cut into small pieces of about 1sq-cm using a diamond scribe to fit inside the sample holder. The sample was then immersed in an electrolyte solution that was cooled to 19°C. The silicon substrate, which acts as the anode, was connected to the positive terminal of the power supply. A platinum mesh immersed in the electrolyte was used as the cathode. The solution was stirred continuously to prevent heat build up at the aluminum/electrolyte interface during the anodization process.

As explained earlier, the pH of the electrolyte plays an important role in the pore geometry. Typical electrolytes used in this project are shown below.

0.3M oxalic acid: 36 ml of Oxalic acid Solution + 1000ml of DI water
2% Sulfuric acid: 20 ml of Sulfuric acid Solution + 1000ml of DI water
10% Sulfuric acid: 100 ml of Sulfuric acid Solution + 1000ml of DI water.
Anodization can be carried out under constant current and constant voltage conditions. For constant current anodization, the voltage drop across the anode and the cathode is recorded to monitor the anodization process. For constant voltage anodization, the current flowing between the anode and the cathode is recorded to monitor the anodization process.

4.1 Anodization using 2% Sulfuric acid and 1% Citric acid

Anodization was carried out on Al/Ta bilayer deposited on Si substrate. The first step of anodization was carried out in 2% sulfuric acid at 1°C, using a current density of 40mA/cm². The anodization was performed until all the aluminum film was consumed and the tantalum layer was reached. The voltage-time relationship monitored during anodization is shown in Fig 4.1. The increase in the voltage after 30sec indicates that all the aluminum was anodized and the tantalum layer was reached. The pores were widened in 3.6% phosphoric acid solution for 5 mins. Figures 4.2 and 4.3 show the cross-sectional views of the sample at different magnifications. As can be seen, the anodization was stopped exactly when the tantalum layer was reached and the oxidation of tantalum layers has just begun. Since the samples were pore widened, the barrier layer is not visible as expected. The template is also not periodic because a single step anodization was used. As mentioned earlier, the periodicity of the template can be improved by using a two step anodization process.
Figure 4- 1 Voltage time relationship obtained during anodization in 2% sulfuric acid at a current density of 40mA/cm$^2$.

Figure 4- 2 Cross sectional view of the Al/Ta bilayer anodized in sulfuric acid at a current density of 40mA/cm$^2$. 

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Reanodization was performed in 1% citric acid solution at 1°C using a current density of 0.5mA/cm² and 1.5mA/cm². The voltage time relationship for anodization using 0.5mA/cm² was given in Fig 4.4. The anodization was carried out for 250 secs on both the samples. The alumina template was etched using the chromic acid solution. The samples were thoroughly cleaned and using DI water and imaged using JOEL- 5600 SEM. The growth of tantalum oxide pillars inside the alumina template was expected. The top view of the samples is shown in Fig 4.5 and 4.7 and the cross sectional view is given in fig 4.6 and 4.8. As seen from the Fig 4.6 & fig 4.8 the pillar growth was not substantial, it is only 20-30nm. Hence they cannot be used to do the next processing step of RIE to make Si quantum wires.
Figure 4-4 Voltage time relationship obtained using 1% citric acid at a current density of 0.5 mA/cm² @ 1°C.

Figure 4-5 Top view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5 mA/cm².
Figure 4-6 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm²

Figure 4-7 Top view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 1.5mA/cm²
Figure 4-8 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 1.5mA/cm²

4.2 Anodization using 0.3M Oxalic acid and 1% Citric acid

Anodization was also performed on the samples in 0.3M oxalic acid solution using a current density of 40mA/cm² @ 1°C. The anodization was carried out until all the aluminum film was consumed and the tantalum layer was reached. The voltage time relationship monitored during anodization is shown in fig 4.9. The increase in the voltage after 22sec indicates that all the aluminum was anodized and the tantalum layer was contacted. The pores were widened in 3.6% phosphoric acid solution for 5 mins.
Figure 4-9 Voltage time relationship obtained using 0.3M Oxalic acid with a current density of 40mA/cm$^2$

Figures 4.10 and 4.11 show the top and cross sectional views of the sample. It can be seen from the figures that the pore diameter is around 50-60 nm, larger than the pores obtained for sulfuric acid. The barrier layer is not visible since it was completely etched during the pore widening step.
Figure 4-10 Top view of the sample anodized in 0.3M oxalic acid at a current density of 40mA/cm²

Figure 4-11 Cross sectional view of the Al/Ta bilayer anodized in 0.3M Oxalic acid at a current density of 40mA/cm²
Reanodization was performed in 1% citric acid solution at 1°C using a current density of 0.5mA/cm². The voltage time relationship for anodization using 0.5mA/cm² is shown in fig 4.12. The anodization was carried out for 70 secs on both the samples. The alumina template was etched using the chromic acid solution. The samples were thoroughly cleaned using DI water and imaged using JOEL- 5600 SEM. The growth of tantalum oxide pillars inside the alumina template was expected. The top view of the sample is shown in Fig 4.13 and the cross sectional views are given in fig 4.14 and 4.15. As can be seen from the Fig 4.14 & 4.15, the pillar growth is not substantial, it is only around 20-30nm. Pillars of substantially larger heights will be required for use as RIE etch masks.

Figure 4-12 Voltage time relationship obtained using 1% citric acid at a current density of 0.5 mA/cm² @ 1°C
Figure 4-13 Top view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm²

Figure 4-14 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm²
Figure 4-15 Cross sectional view of the tantalum oxide pillars anodized in 1% citric acid at a current density of 0.5mA/cm²

4.3 Anodization in 10% Sulfuric acid and 1% Citric acid

The lack of vertical growth of tantalum oxide pillars can be attributed to several factors, concentration of the electrolyte, low current density during reanodization, temperature of the electrolyte and also time of anodization. A careful investigation on the process parameters was done and the conditions of anodization and reanodization were changed. The anodization was carried out in 10% sulfuric acid using a constant current density of 20mA/cm² at 19°C. Figure 4.16 gives the voltage time relationship obtained during this process. The samples were then pore widened in phosphoric acid solution for 15 mins. Reanodization was done in 1% citric acid solution using a current density of 4mA/cm². This is done for over 600 sec and the process was stopped. Figure 4.17 gives the voltage time relationship obtained during this process. The alumina template was
etched using the chromic acid solution and the samples were thoroughly cleaned in DI water. The image of the sample are taken using a JEOL-SEM. Figures 4.18 and 4.19, shows the top and cross sectional views of the sample. The height of the oxide pillars was estimated to be about 65-75nm. The growth rate was calculated to be 0.135-0.156 nm/sec.

![Graph](image1)

Figure 4-16 Voltage Time Characteristics obtained during constant current anodization done in 10% sulfuric acid @19°C

![Graph](image2)

Figure 4-17 Voltage Time Characteristics obtained during constant current anodization done in 1% citric acid @19°C
Figure 4-18 Top view of the tantalum oxide pillars on Silicon Substrate

Figure 4-19 Cross section of the Tantalum oxide pillars on Silicon substrate
CHAPTER 5

CONCLUSION AND FUTURE WORK

This thesis described the operational principles, design procedures and the implementation of quantum wire photodetectors in the long and very long wavelength regions. The infrared photodetectors are based on intersubband transitions in semiconductor quantum wires and have the potential for higher operational temperature, increased signal-to-noise ratio, reduced dark current, wider spectral range and sensitivity to normal incident radiation. The quantum wire IR detectors were implemented using a nonlithographic nanostructure fabrication technique that is capable of producing large arrays of semiconductor quantum wires of a variety of materials as well as on a variety of substrates. A more detailed analysis can be carried out on the process parameters to yield better periodicity of the pillars. The process parameters for the RIE of tantalum oxide must be found to complete the fabrication of IR detectors.
REFERENCES


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