# Removal of metal oxide defects through improved semi-anisotropic wet etching process

by

Neha H. Dave

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Author.............................................................................................
Neha H. Dave
Department of Mechanical Engineering
August 10, 2012

Certified by.............................................................................................
Jung-Hoon Chun
Professor of Mechanical Engineering
Thesis Advisor

Accepted by.............................................................................................
David E. Hardt
Professor of Mechanical Engineering
Chairman, Department Committee on Graduate Students

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## Abstract

Data recently collected from an industrial thin film manufacturer indicate that almost 8% of devices are rejected due to excess metal, or unwanted metal on the device surface. Experimentation and analysis suggest that almost half of these defects are caused by incomplete removal of nickel oxides that form on top of the conductive nickel surface throughout the heated environment of the upstream process. This study classified and identified the composition of these excess metal defects, evaluated recommended wet etch methods to remove nickel oxide, and finally proposes a wet etch process that will rapidly remove defects while continuing to maintain the desired semi-anisotropic etch profile, uncharacteristic of most wet immersion etch processes. Results attested that rapid exposure to dilute (40%) nitric acid followed by immediate immersion into a cleaning agent, proprietary nickel etchant, and titanium tungsten etchant removed all nickel oxide defects. Upon implementation, this method has the potential to reduce scrap due to excess metal by 3% and reduce overall etch process time by 25%. In addition, a process was developed to completely etch patterned substrates with high defect density mid process and rework them from raw substrates.

**Thesis Supervisor:** Dr. Jung-Hoon Chun
**Title:** Professor of Mechanical Engineering

# Acknowledgements

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To my parents and grandparents- thank you for inspiring and encouraging me to do what I love and for always nudging me in the right direction. To my sister- you know me better than I know myself and will forever be a role model to me.

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# Chapter 1: Introduction

Thin film devices act as small scale circuits, manufactured on a ceramic surface with wiring 'printed' onto the surface in specific patterns. Devices are manufactured using a series of additive and subtractive processes performed on a mechanically flexible piezoelectric ceramic. During application, electrical current moves smoothly through these metal surfaces, possible only if the metal pathway is clear. Any misplaced metal or contaminants found on the surface can reduce or block the flow of current through the circuit. Thus, high quality devices will not contain any surface or material defects. This study identified and eliminated the key contributors of reoccurring surface and material defects that reduce the manufacturing yield of thin film devices.

## 1.1 Motivation

Currently, 16.2% percent of devices are rejected from a combination of excess metal defects, holes or voids in the pattern, or cracks and breaks in the ceramic material. Each lost device results in wasted material, labor time, and cost, while any reduction in yield loss will correspond to a significant increase in revenues for the company. The goal of this yield improvement initiative is to eliminate a significant percentage of excess metal, voids, breakage defects. In the distribution of yield loss, provided in Figure 1, devices are categorized according to the most visible defect. In addition, historical data indicate that less than 15% of rejected devices contain multiple defects, and therefore this distribution is an accurate representation of the frequency of all defects.

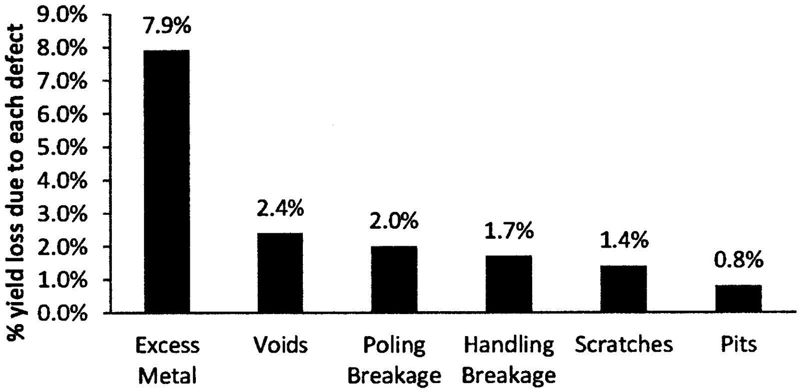

*Figure 1: Primary defects in 2011*

## 1.2 Objectives

The principal objective of this project was to identify and eliminate the causes of defects with significant contribution to yield loss and increase the manufacturing yield. In order to achieve this improvement, the project was divided into three separate goals, each established to target a leading cause of defective devices. These goals were:

1. Eliminate excess metal defects due to incomplete metal and oxide removal
2. Eliminate excess metal defects and pattern voids due to defective photoresist coating
3. Eliminate substrate breakage caused during the poling process

## 1.3 Process Overview

The manufacturing process for lead zirconate titanate (PZT) thin film devices is initiated by coating the substrates, or ceramic wafers, with two metal layers. First, a single barrier layer of titanium tungsten (WTi) is deposited across the entire surface to promote its adhesion to the conductive metal layer. The substrate is then sputtered with a layer of nickel (Ni) which will carry current through the device. The material then undergoes a process called poling, which will change its molecular orientation to improve its piezoelectric properties.

The process of coating, imaging, exposing, and etching substrates to produce a metal pattern is collectively known as photolithography. During this process, the metalized substrates are sprayed with a protective photoresist layer. A mask with an image of the pattern is then placed on top of each substrate while it is exposed beneath a patterned mask to high intensity ultraviolet light. Any photoresist that was not shielded by the mask from the UV light will dissolve in the developing bath, leaving behind a pattern of intact photoresist in the shape of the circuit wiring. A wet etch process is then performed to remove metal in the non-patterned areas. At the end of the photolithography stage, the devices are electrically functional but still connected to each other on the substrate. To separate them, the substrates are diced into individual devices for final testing and application.

Throughout the manufacturing process, a number of visual and electrical quality inspections take place to quickly identify process control concerns. Reject devices are typically eliminated in the final inspection stage in order to conserve the other devices on the substrate. Once the operators have verified the electrical and visual quality of all devices, the devices are carefully packaged and sent to the customers. Figure 2 outlines this high volume manufacturing process, as well as the basic function and primary source of yield loss at each stage.

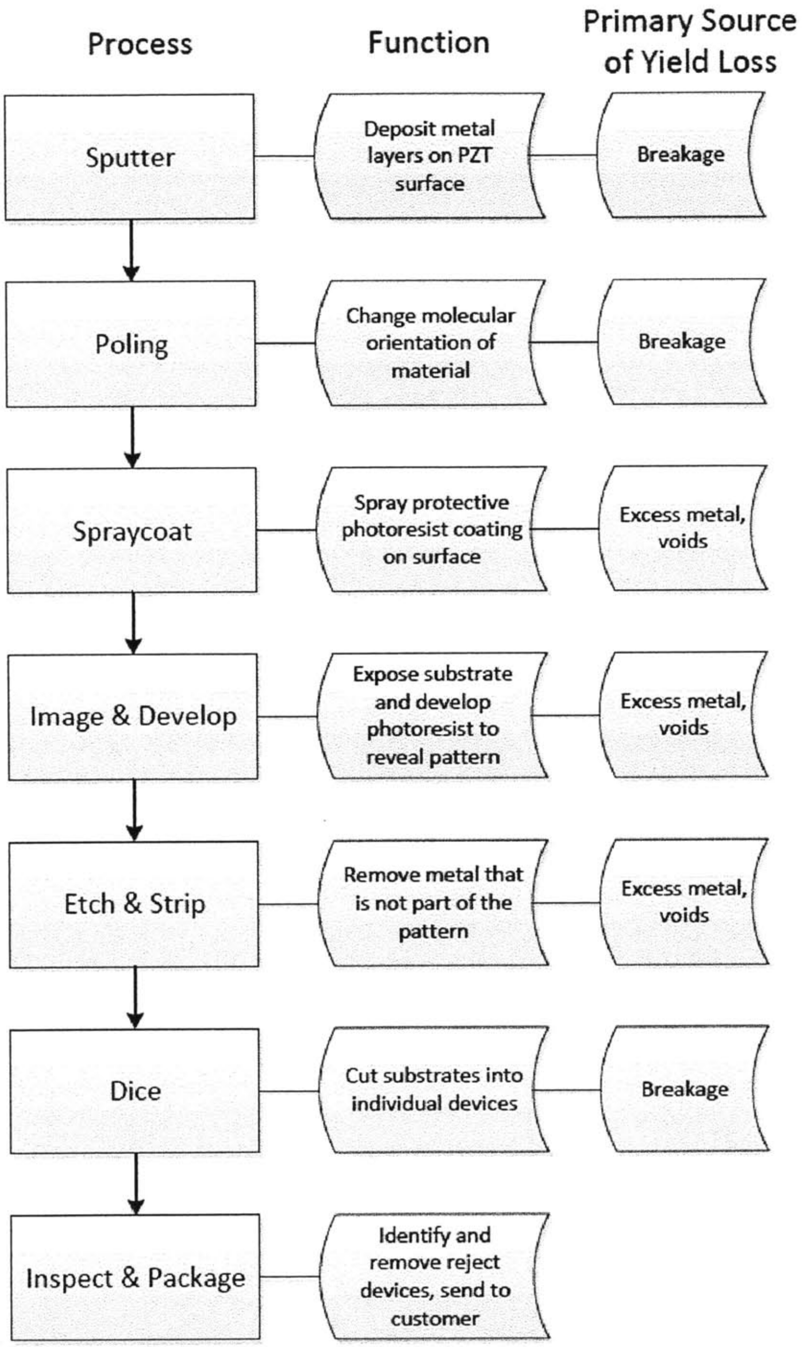

*Figure 2: Outline of manufacturing process for PZT thin films*

## 1.4 Defect Classification

At the start of this project, it was necessary to classify the surface defects and evaluate specific process causes to target. Four thousand devices were manufactured according to the standard process in order to generate a set of controlled defect data. This set of devices produced 321 defects, with 50% rejected due to excess metal. Following a careful inspection, all excess metal defects were classified according to shape, composition, and size, as shown in Figure 3.

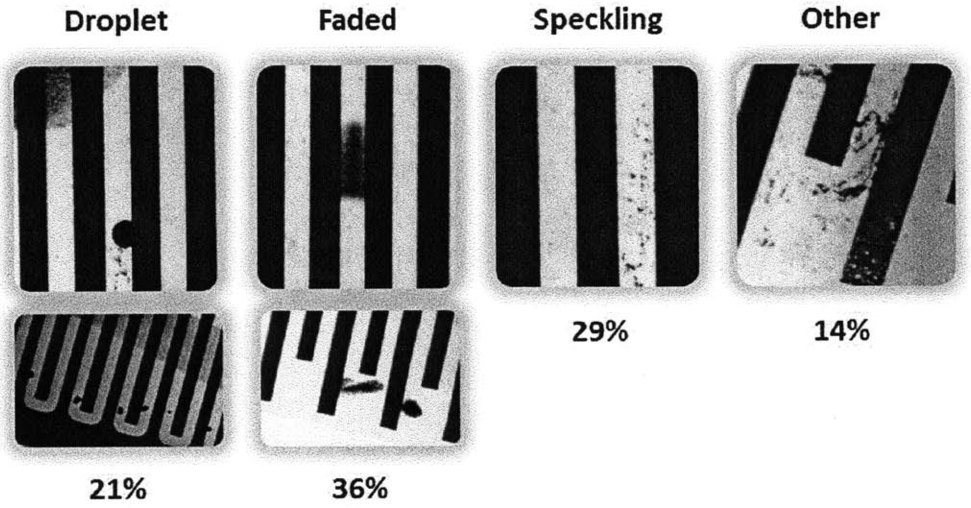

*Figure 3: Classification of excess metal defects, where the gap between the lines is approximately 125 microns*

It was hypothesized that the majority of excess metal defects and voids are generated during two upstream processes: spray coating and etching. Thus, these processes were targeted in order to eliminate yield loss due to excess metal. Breakage, a separate contributor to yield loss because of its ability to destroy an entire substrate of devices, was also analyzed as it related to both machine and handling errors.

In order to approach all factors that contribute to yield loss and subsequently reduce this loss, it was necessary to divide the project and target three individual process steps. For each activity, one team member was responsible for root cause analysis, experimentation, data generation, and finally implementation. Jun Bum Lee [1] explored excess metal and void defects caused by defective photoresist quality, while this author aimed to reduce these defects as they related to etching. Abdulelah AlSaeed [2] researched the root cause of breakage inside the poling machine. All team members shared the underlying goal of yield improvement.

The contents of this thesis summarize work that relates to the etching process only.

# Chapter 2: Background and Literature Review

The goal of this project was to eliminate any excess metal defects that are caused by incomplete metal removal during the etching process. Currently in place is a wet etch process, designed to rapidly remove metal layers while maintaining device circuitry dimensions. Chapter 2 provides a brief background on the types of etching processes and methods commonly used in industry, specific characteristics of wet etching, and the factors that affect the quality of the process. A summary of the specific procedure used for PZT thin film devices follows this research.

## 2.1 Introduction to Etching

Etching during thin film manufacturing is a subtractive process which chemically removes metal layers from the surface of a substrate or wafer. Etch processes are designed to only remove metal layers that are exposed to the etchant. Etching is an electrochemical process, and thus uses electron transfer to achieve the desired surface reaction. As a result of this electrochemical reaction, metal that is not covered with photoresist is removed, leaving a clear pattern of conductive metal. Figure 4 shows the locations where metal would be etched away during a complete etch process.

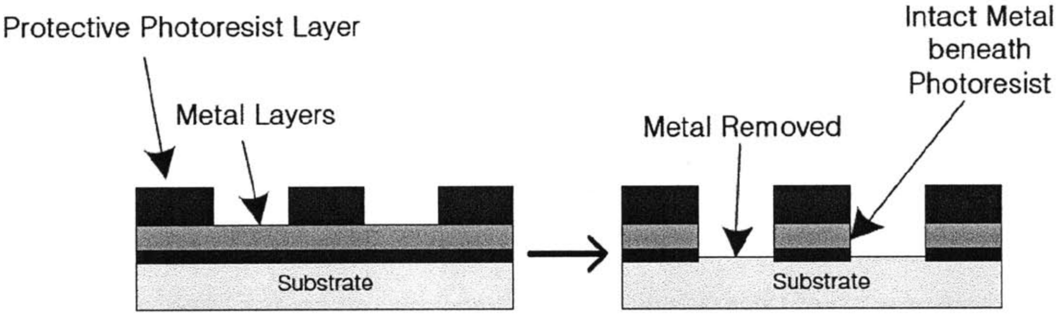

*Figure 4: Location of etching when photoresist layer protects pattern (cross section)*

Etching can be categorized according to the medium used to etch, direction of etch rate, and specific reaction that occurs. During wet etching, substrates are immersed in liquid chemicals which form the surface reaction and dissolve the metal surface. In dry etching, substrates are etched by plasma.

Isotropic etching occurs when the etch rate is the same in all directions, i.e. the lateral etch rate is equal to the vertical etch rate. Typically, isotropic etching is best achieved with wet etching, as the chemicals will completely surround the surface. During anisotropic etching, typically achieved with a dry etch process, the material removal rate depends on the crystalline orientation of the surface planes [3]. Figure 5 shows the surface profile resulting from isotropic and anisotropic etching processes.

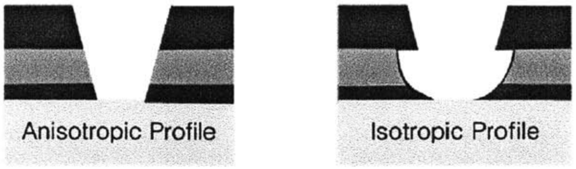

*Figure 5: Cross sections of a complete anisotropic and complete isotropic etch profiles*

The source company for all data currently uses lead zirconate titanate (PZT) as the substrate for its thin film manufacturing process. The devices that are produced have a single electronic pattern layer on their surface. On this side, metal must be removed in locations not covered by photoresist. However, substrates are initially coated with metal on both the front and the back in order to meet the requirements for poling. There is no photoresist layer on the back side, and therefore the entire back surface of metal is removed during etching.

The current etch process removes metal on PZT surfaces with a series of wet chemical baths, designed to produce a semi-anisotropic etch profile. The lateral etch rate is controlled in order to minimize undercutting of the protective photoresist layer, but the vertical etch rate is maximized to remove metal quickly. The desired etch profile for this type of device is shown in Figure 6. As Figure 6 shows, the metal layers are completely removed in locations where photoresist is not present, but there is no lateral etching of the metal layers beneath the photoresist.

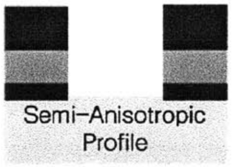

*Figure 6: Semi-anisotropic etch profile for PZT thin films*

Devices are inspected before and after etching to achieve accurate patterns and complete metal removal. For complete device functionality, a semi-anisotropic etch profile is desired.

Section 2.2 describes the specific cleaning and etching processes that are currently used.

## 2.2 Standard Procedure

### *Cleaning:*

Prior to etching, substrates are immersed in a gentle cleaning bath which combines sodium metabisulfate, trisodium nitrilotriacetate, alkyl aromatic salt, and anionic surfactant as its active ingredients. This cleaner is intended to remove native oxides and particles or oils that remain on the surface. Substrates are then placed into an overflow bath to rinse off detergent residues.

### *Nickel Etching:*

The first etching step removes only the pure Ni layer, at an etch rate of .015 microns per second. This is achieved with a heated bath of dilute sulfuric acid ($H_2SO_4$) and phosphoric acid ($H_3PO_4$) to dissolve the metalized surface. Etch rate is managed by temperature and rotational agitation, both controlled within the bath using a Cole Parmer® Stabletemp hot plate fitted with a magnetic stirring system. Etching operators will also raise and lower the boat of substrates to attain vertical agitation and adequate supply of fresh chemicals to the surface of each substrate.

### *Titanium Tungsten Etching:*

The second etching step aims to remove the WTi adhesion layer that is in direct contact with the PZT surface at a rate of .0004 microns per second. It must be noted that due to the surface roughness of the PZT substrates, the process etch rate will be slower than any predicted or theoretical etch rates for titanium tungsten. As with the nickel etching step, temperature and agitation are controlled to maintain an accurate and repeatable etch rate.

These three sequential steps are shown in the process diagram in Figure 7. All etch processes are highly selective, and are designed to etch only the topmost surface in each bath.

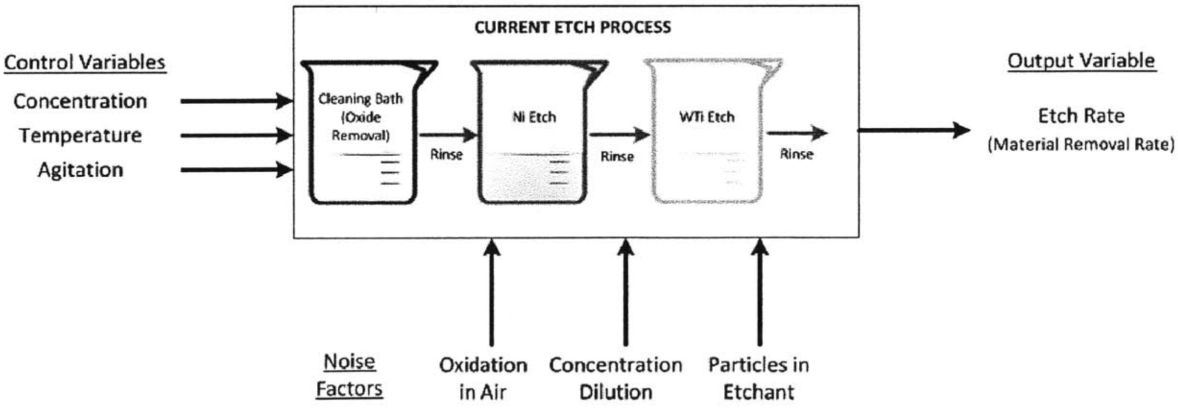

*Figure 7: Current etch process*

## 2.3 Wet Etch

In practice, wet etching is achieved by three sequential steps, as shown in Figure 8 [3].

1. Transport of reactants to the metal surface
2. Surface reaction
3. Transport of products from the surface into the surrounding media

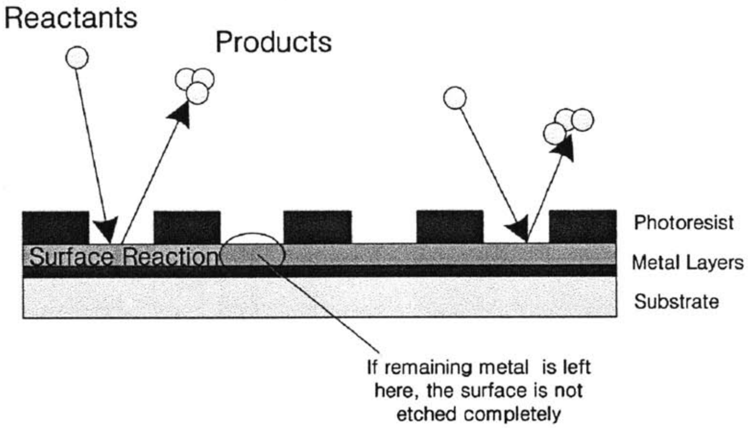

*Figure 8: Cross sectional schematic representation of the etch process*

In order for a wet etchant to function correctly, it requires three key inputs: an oxidizer for electron loss, an acid or base to dissolve the oxidized surface, and a dilutent medium to facilitate the transport of reactants and products between the surface and the solvent [3].

When the surface reaction occurs at the solid-liquid interface, the binding forces between the solid particles must be overcome so that the components of the solid are transferred into the liquid phase. The solvent molecules form a solvate shell around the dissolved particle, and are able to move within the solvent. Standard etch processes use water as the solvent, thus creating a hydrate shell around dissolved molecules [4].

As Figure 8 shows, the etch process must remove all metal that is not covered with photoresist. Metal remaining in exposed areas is a clear indication of a fault in the etch process. The cause of this fault could be any of the following:

1. Incomplete surface reaction
2. Insufficient time in the etchant
3. Insufficient transport between reactants and surface
4. Weak etchant that is unable to dissolve material
5. Contaminants preventing the metal layers from being etched

## 2.4 Surface Condition Prior to Etching

The etch rate and quality is dependent on the condition of the surface to be etched. Surface contaminations such as particles or other impurities can alter the etch rate. For example, a reduced etch rate could result if surface contaminants resist the etchant or merely etch at a slower rate, preventing the metal layers beneath from being fully removed. With increased time in the etchant to compensate for this slow etch rate, variations in line width and roughness would be observed, as shown in Figure 9 [4].

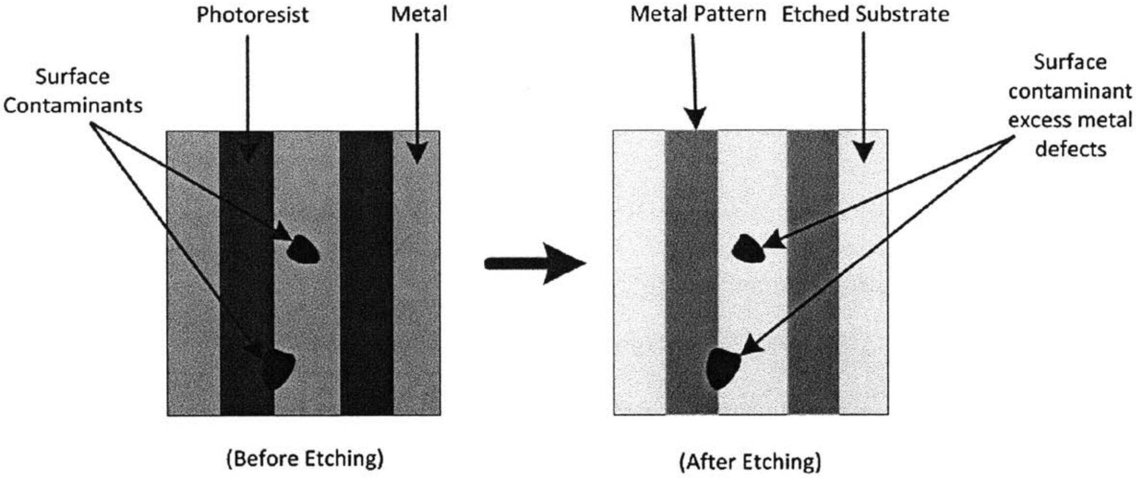

*Figure 9: Effect of surface contaminants on device pattern*

Similarly, an increased etch rate could reduce the quality of the metal pattern of the device. Though the photoresist layer is designed to withstand the surface reaction caused by the etchant, it may naturally decay with too much time in the chemicals, as shown in Figure 10.

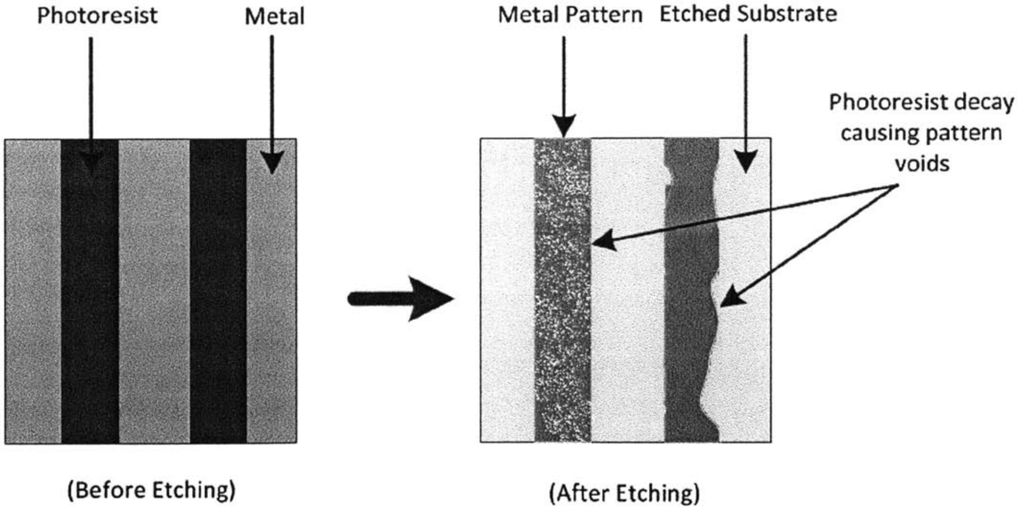

*Figure 10: Effect of photoresist decay on device pattern due to overetching*

Furthermore, because wet etching is primarily isotropic, a lateral etch rate that is too rapid will result in undercutting, or etching beneath the photoresist layers, of the line. This effect is shown in Figure 11.

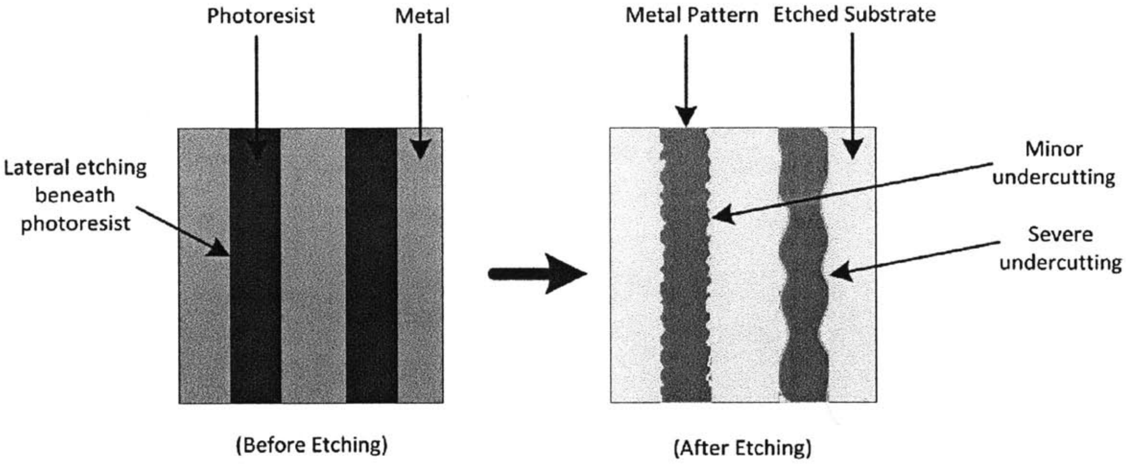

*Figure 11: Effect of increased lateral etch rate on device pattern*

A particle located beneath or within the photoresist layer may be covered by a thinner layer of photoresist that can break down with less chemical exposure or may etch away, leaving behind a spot without photoresist coverage. As this exposed metal is etched, a void, or hole in the pattern, is revealed as shown in Figure 12.

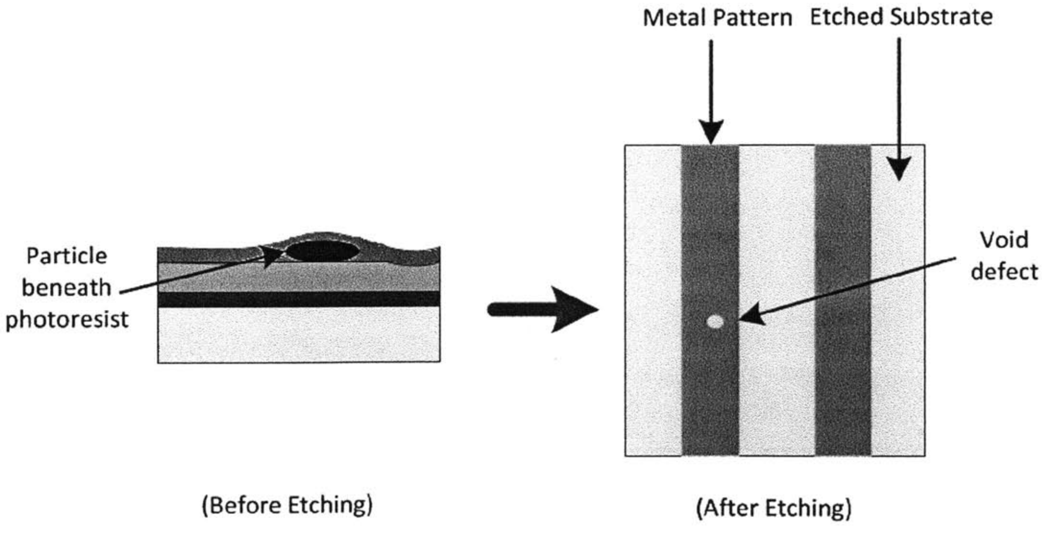

*Figure 12: Effect of particle contaminants on final device*

The surface condition of all materials during etching is also affected by the interaction between the material and the reactive components of the surrounding atmosphere. For example, air and atmospheric water vapor will always surround the material and are likely to react with the surface even at room temperature. These surface reactions tend to advance corrosion or buildup of passivating films, often in the form of metal oxides [4]. Similarly, carbon dioxide, which makes up 0.035% of pure air, will react with the surface in a neutral or low acid environment to form carbonates at the surface. Sulphur dioxide from unfiltered air and hydrogen sulphide created by human presence may form sulphide contaminations on the metal surface. This type of contamination is rarely soluble in a simple rinsing process, and may require an additional process step for complete removal [4].

The surface condition of material to be etched can also be compromised by the composition of the solvents used to etch and rinse semiconductor devices. For example, acidic or basic reacting gases, often found in polluted air, are soluble in water and thus will accumulate as salts, complexes, oxides, and hydroxides within the surface films of water based solvents and rinses. These surface films will thicken with additional exposure to the atmosphere, higher temperature, or increased humidity, and may hamper the reaction of the etchant [4]. In summary, any reaction between the atmosphere and the material can cause surface layers to etch at a slower rate, preventing etching of the pure sputtered metal layers and leading to excess metal defects.

In areas with high particle concentration, it is necessary to minimize the surface contamination of material prior to etching with a cleaning process. In order to remove loose sticking particles, substrates should be sprayed with particle-free compressed air or a clean inert gas. Mechanical cleaning can also be achieved with a high pressure liquid method or by scrubbing.

When substrates are washed in detergents to remove organic particles or films, small amounts of impurities that are dissolved tend to stay at the surface by preferential molecular interaction with surface atoms or as residues by evaporation of the solvent. Cascade baths can minimize, but not eliminate, these residual pollutions due to the diminishing residual concentration within the cascade from bath to bath. However, when several substrates are cleaned in the same cascade, residuals can also start to accumulate or absorb into the rinse, spreading the pollutions from previous substrates onto future ones. If residual accumulation is a characteristic of the manufacturing process, it may be necessary to use a more aggressive cleaning method. Thus, sulphuric acid or hydrogen peroxide is often used to clean substrate surfaces [4]. Though cleaning may add an additional step to the wet etch process, this is an essential step to improve the quality of the substrate surface and allow the etch surface reaction to proceed effectively.

## 2.5 Etch Rate

Etching is just one part of the thin film manufacturing process, and must be accomplished at the maximum rate possible while maintaining the correct line width and definition. Industry methods typically work towards a wet immersion etch time on the scale of 1 minute in order to ensure adequate controllability and reproducibility of the etch process and accurately remove contamination, metal, and any other residues. Similarly, the etch rate of layers beneath the intended metal to etch should be minimized. This ability of a chemical to etch only one layer at a time is defined by etching selectivity, and discussed in Section 2.6 [4].

The capability of an etchant to remove layers at the desired etch rate is determined by three key factors: the temperature of the etchant, the concentration of the etchant, and the agitation or transport mechanism inside the immersion tank. In order to produce a high quality etch profile, it is necessary to optimize the combination of these factors, because an increase in any one factor will drastically increase the etch rate. These variables are thus treated as controllable inputs, as shown in Figure 13.

As mentioned in reference to the surface condition of material prior to etching, particulates or contaminants can also decrease the etch rate of a metal layer. Oxidation may also occur in the air, accumulating with increased exposure to the atmosphere. As substrates are repeatedly etched in a chemical bath, the products of the reaction will also build up in the surrounding solvent. These factors can be treated as noise factors, as shown in Figure 13, for the etch process, which should be minimized but are not typically controlled as a process input.

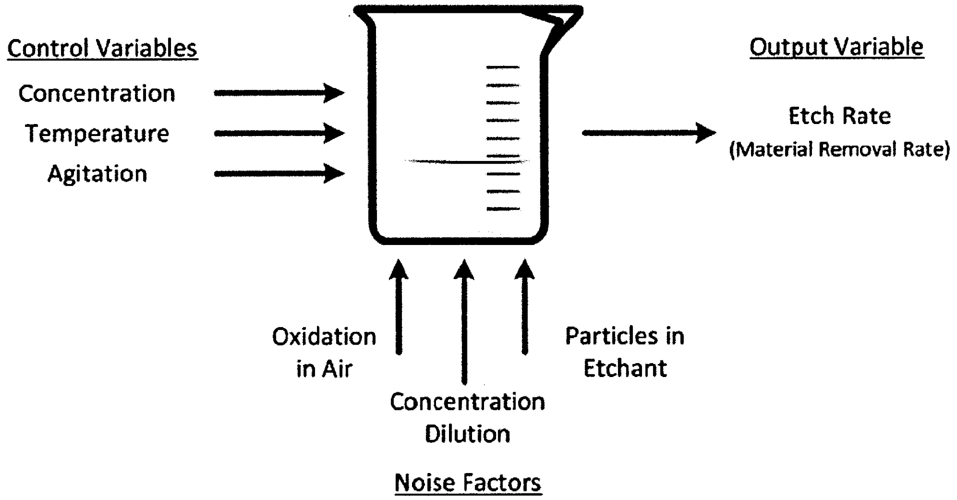

*Figure 13: Variables that affect etch rate*

The etch rate, r, for each metal layer can be estimated using the etched thickness, $d_{etch}$, and etching time, $t_{etch}$, as follows [4].

$$r = \frac{d_{etch}}{t_{etch}} \tag{1}$$

As shown in this equation, any variation in thickness measurement can affect its accuracy. Though the etched mass can be determined by weighing, the surface layer typically comprises less than 0.1% of the substrate mass, and weight measurements may have high relative error. Instead, etch rate is often estimated by measuring the current density of an etched substrate. According to Faraday's laws, the absolute etched mass of a material in electrochemical etching is equivalent to its charge. Thus, the current density, or current per unit area, can be used to compute the surface current. This current corresponds to the quantity of material etched per unit time, and the etch rate can be estimated from the electrochemical valency of the material [4].

## 2.6 Etching Selectivity

Selective etching is an etch process during which one material is etched rapidly while a different material is etched very slowly or not at all. In an ideal etch process, each etchant will only react with one surface layer. However, many etchants are known to react with several layers, but react more or less selectively with different materials. In order to achieve a high etch selectivity, it is necessary to select etchants that will not attack the lower metal layers or the surface of a substrate. Wet etching processes are known to be highly selective with respect to metal layers, due to the ability to predict and control the surface reaction that will take place upon substrate immersion.

## 2.7 Etch Rate Uniformity

A defect that is located on any section of a substrate can cause one or several devices to be rejected. Thus, the etch rate must be uniform across a substrate, from substrate to substrate, between work orders, and regardless of feature size or pattern density. Etch rate uniformity can be estimated with (2), where 100% etch rate uniformity suggests that the etch rate is independent of placement on the substrate or chemical dilution with time. 0% etch rate uniformity may denote that an etch process is insufficiently supplying fresh chemicals to the entire substrate or that the concentration of reaction products within the etchant is too high. 100% etch rate uniformity is desired.

$$Etch\ rate\ uniformity\ (\%) = \frac{maximum\ etch\ rate - minimum\ etch\ rate}{maximum\ etch\ rate + minimum\ etch\ rate}\ x\ 100\% \qquad (2)$$

Figure 14 shows a nonuniform etch rate across a substrate. This type of process may have remaining metal on some or all devices.

*Figure 14: Nonuniformity on substrate surface*

Figure 15 displays a nonuniform etch rate between substrates, indicating that the etch bath does not always adequately bring fresh chemicals to the substrate surface or that the etch process is not consistent [6].

*Figure 15: Nonuniformity between substrates*

## 2.8 Known Etchants

### *2.8.1 Nickel*

The manufacturing process for these thin films requires a conductive layer of pure nickel patterned onto a PZT substrate. The following formulations in Table 1 have been experimentally verified to etch pure nickel under the described conditions [7]:

*Table 1: List of known nickel etchants*

| Name | Composition | Time | Temperature | Comments |
|---|---|---|---|---|
| | 30% $HNO_3$<br>10% $H_2SO_4$<br>50% HAc<br>10% $H_20$ | 30 seconds | 85 | Polishing properties |
| **Dilute Sulfuric Acid** | 57% $H_2SO_4$<br>43% $H_20$ | 2 min | RT | Polishing properties |
| **Dilute Nitric Acid** | 30% $HNO_3$<br>70% $H_20$ | 1 min | RT | Prevents formation of Nickel Oxide |
| | 50% $HNO_3$<br>50% $CH_3COOH(HAc)$ | | RT | Removal etch |
| | 20g $Ce(NH_4)_2(NO_3)_6$<br>200ml $H_20$ | | RT | Removal and patterning etch |
| **Jewitt-Wise Etch** | 10% $NH_4(H_2SO_4)_2$<br>10% KCN | | | |
| | 10% HCl<br>33% $HNO_3$<br>67% $H_20$ | | | Clean Nickel Surfaces |
| **Hyrofluoric Acid** | HF | | | Slow etchant |
| **Phosphoric Acid** | $H_3PO_4$ | | | Slow etchant |
| **Nitric Acid** | $HNO_3$ | | RT | Extremely rapid |
| **Nitric Acid + Hydrofluoric Acid** | HF<br>$HNO_3$ | | | Increased HF will reduce removal rate for controllability |
| **Meta-phosphoric acid** | $HPO_3$ | | RT | Slow etch, can be mixed with alcohol |
| **Aqua Regia, Modified** | $H_20$<br>4 HCl<br>1 $HNO_3$ | | RT | Increased HNO3 will increase etch rate |
| | 30% $FeCl_3$ | 2-10 min | Warm (60 °C) | |
| | 45% $H_2O_2$<br>10% HCOOH<br>45% $H_20$ | 10-20 min | 50-60 °C or 65-70 °C | Surface cleaning properties |
| | 50g $2NH_4NO_3.Ce(NO_3)_3.4H_2O$<br>10 ml $HNO_3$<br>150 ml $H_2O$ | 60-90 seconds | RT | Increased HNO3 will reduce etch rate |

| Name | Composition | Time | Temperature | Comments |
|---|---|---|---|---|
|  | $H_2SO_4$<br>$D_2O$ |  |  |  |
|  | $NH_4Cl$<br>$NH_2CONH_2$ |  | 120-135 °C | Polishing properties |
|  | 30% $HNO_3$<br>10% $H_2SO_4$<br>10% $H_3PO_4$<br>50% HAc | 30-60 seconds | 85-95 °C | Polish etch |
| **Methyl Alcohol** | MeOH |  | RT | Cleaning of Nickel Surface |
|  | 2 oz $NaCO_3$<br>5 oz $Na_2SiO_9$<br>0.5 oz NaOH | 1-2 min | 99 °C | Electropolish and final cleaning |
|  | 2 oz $NaCO_3$<br>1000 ml $H_2O$ | 1-2 min | 120 °C | Electropolish etchant |
|  | 453.6 g $H_3PO_4$<br>185.6 g $Al_2(SO_4)_3.18H_2O$ | 5 min | 80 °C | Electropolish etchant |

Research has established pattern transfer by etching in a heated (35-50 °C) bath with the following composition:

1. Concentrated sulphuric acid ($H_2SO_4$)
2. 30% hydrogen peroxide ($H_2O_2$)
3. Concentrated phosphoric acid ($H_3PO_4$)
4. 30% Aqueous solution of nickel sulfate ($NiSO_4$)

The experimental etch rate for this isotropic etchant was .0075 microns/second, and it proved to be highly selective towards nickel while leaving the surrounding gold surfaces intact [8].

Commercial nickel etchants are also available to etch pure nickel and any native oxides that may form at the surface. Transene, a local electronics company, sells a formulation called Nickel Etchant TFB, which is shown to exhibit for controlled removal of evaporated nickel films and good compatibility with all types of photoresist. Transene recommends that this etchant be used at 25 °C in order to etch a film thickness of .15 microns at .003 microns per second [9]. According to the manufacturer, the etch rate of a nickel surface will double with each 10 degree increase in temperature, as shown in Figure 16.

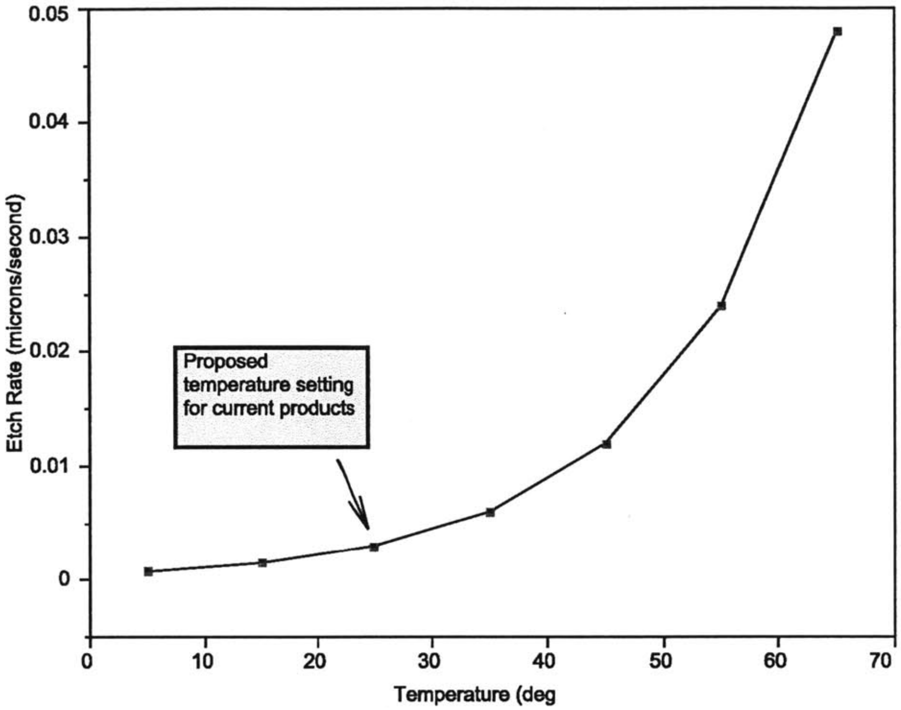

*Figure 16: Estimated etch rate for Transene Nickel Etchant TFB*

### *2.8.2 Nickel Oxide*

Nickel oxide (NiO) often forms on pure nickel surfaces with extended exposure to the atmosphere or aqueous solutions. However, it has no use in industry beyond normal surface passivation as a native oxide. Thus, NiO is often considered a contaminant in device fabrication, and should be removed prior to etching [7]. Table 2 describes etchants commonly used to remove NiO surface layers:

*Table 2: List of known NiO etchants*

| Name | Composition | Time | Temperature (°C) | Comments |
|---|---|---|---|---|
| **Ammonium Hydroxide** | $NH_4OH$ | Seconds | RT | Removes native oxides but does not etch pure nickel |
| **Nitric Acid** | $HNO_3$ |  | Hot |  |

Commercial cleansing agents are also available to remove native oxides from any surface. For example, the Dow® Chemical Company sells a cleaner consisting of sodium metabisulfate, trisodium nitrilotriacetate, alkyl aromatic salt, and anionic surfactant. This solution has been experimentally verified using PZT substrates sputtered with nickel and subject to NiO growth.

### *2.8.3 Titanium Tungsten*

WTi is often used as a blocking layer against diffusion and reaction of other metals into the substrate material's surface. For thin film fabrication, it is also used as an adhesion layer between the pure nickel and the PZT substrate. Like the conductive layer, it must be patterned and removed during the etching process. Table 3 includes commonly used WTi etchants [7].

*Table 3: List of tested WTi Etchants*

| Name | Composition | Time | Temperature (°C) | Comments |
|---|---|---|---|---|
| **Hydrogen Peroxide** | $H_2O_2$ | < 1 hour | RT | Removes bulk WTi |
| **Dilute Ammonium Hydroxide** | 33% $NH_4OH$<br>67% $H_2O$ | | | Removes WTi thin films |
| **Aqua Regia** | $H_2O$<br>3 HCl<br>1 $HNO_3$ | | | Slow etch rate |

### *2.8.4 Lead Zirconate Titanate*

Thin film application requires that the thickness of the final devices is equal to the original substrate thickness. The customer does not allow the use of etchants that would alter the surface roughness of the PZT substrates. Therefore, it is necessary to verify that no etchants used during manufacturing will etch PZT material.

Limited research is available on chemicals harmful to sintered PZT material. However, one research project at the University of Michigan has developed a method to etch PZT structures to provide uniform wafer surfaces. This study uses two reactions to reduce an 18 micron PZT layer at a rate of 2-3 microns per minute [10].

The following aggressive etchants and their associated reactions were used to etch the PZT surface [10]:

1. Hydrochloric Acid and Hydrofluoric Acid

$$Pb(Ti,Zr)O_3(s) + HCl\ (aq) + HF\ (aq) \rightarrow [TiF_6]^{2-}(aq) + [ZrF_6]^{2-}(aq) + [PbCl_4]^{2-}(aq) + PbClF\ (s) + H_2O\ (l) \quad (3)$$

2. Lead Chloride Fluoride and Nitric Acid

$$PbClF\ (s) + HNO_3(aq) \rightarrow PbCl_2 + Pb^{2+}(aq) + NO_3^-(aq) + HF\ (aq) \quad (4)$$

To avoid metal etching processes that remove PZT surface layers and maintain a process that is approved by the customer, the chemical combinations found above will not be used.

## 2.9 Nickel Oxide Formation

NiO forms rapidly when Ni plated surfaces are introduced to temperatures between 400 °C and 900 °C [11]. However, NiO can also form in both atmospheric and aqueous conditions, even at room temperature.

Room-temperature nickel oxidation at low and atmospheric oxygen pressures was evaluated at pressures from 1 x $10^9$ torr to atmospheric pressure (760 torr). It was experimentally observed that on an atomically clean pure Ni surface, oxidation reactions present a coalesced oxide film on the surface at low vacuum pressures. From this layer, it is possible for NiO to nucleate and grow laterally across the surface, controlled by the rate of oxygen arrival to the surface. As temperature remains at room temperature and atmospheric pressure is reached, the oxides continue to grow, often with logarithmic rates [12].

It was concluded that at higher pressures, there was also an additional surface reaction which led to the formation of hydroxide on the surface. This resulted in a two-structure oxide consisting of nickel hydroxide (Ni(OH)2) at the interface between the air and the oxide surface NiO between the metal and hydroxide layer [12].

A study of temperature and relative humidity on NiO growth was also conducted, citing that at 40 °C, the maximum thickness of native oxides was measured to be 2.8nm after just 2 days. Similarly, for all temperatures measured, an increase in relative humidity caused a significant increase in oxide film thickness. Low relative humidity tended to limit the growth of oxide films, while high relative humidity fueled the oxide growth process. Figures 17 and 18 represent this experimental data [13].

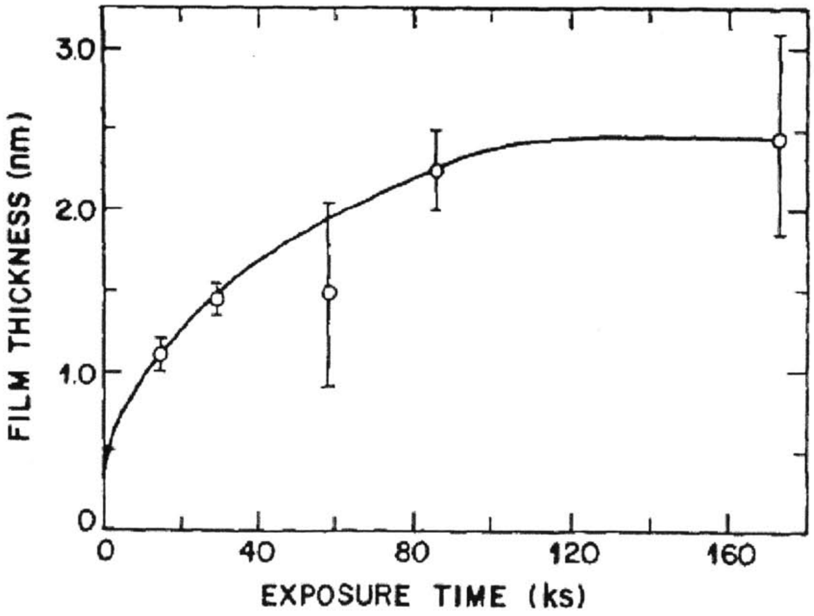

*Figure 17: Tarnish (Oxidation) thickness as a function of exposure time at 40 °C and 95% Relative Humidity [13].*

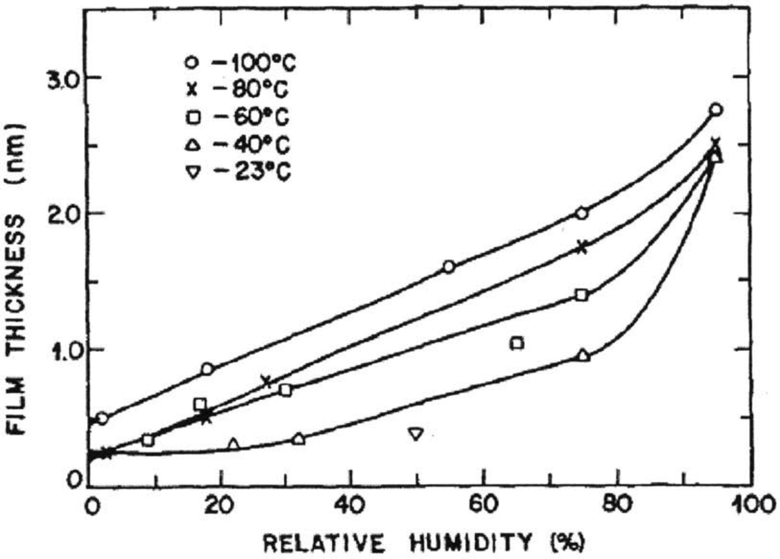

*Figure 18: Tarnish film thickness as a function of relative humidity, with exposure time of 2 days [13].*

The growth of NiO thin films by immersing substrates in a room temperature chemical bath and allowing deposition to take place was also explored. A bath of nickel sulfate, ammonia, and potassium persulfate was prepared and substrates were immersed with stirring rates of 200, 300, and 400 rpm. Results showed an initial introduction phase of the process consisting of no oxide film growth, closely followed by a region of linear film thickness growth, and finally by a region of growth depletion at final film thickness, as shown in Figure 19 [14]. The shape of the curve is similar between stirring rates, but it is clear that an increase in stirring rate does reduce the maximum oxide growth thickness.

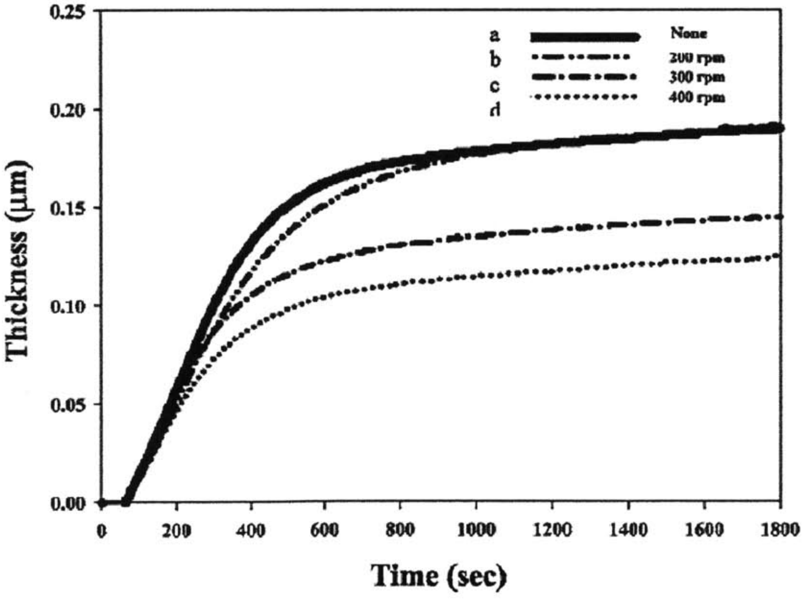

*Figure 19: NiO growth rate in a bath of nickel sulfate, ammonia, and persulfate aqueous solution at room temperature [14].*

# Chapter 3: Experimental Methodology and Results

In order to provide a set of solutions to reduce excess metal defects, several devices were characterized according to the type of excess metal defect and probable cause. The primary theory for this thesis is that faded defects, which contribute to at least 3% of yield loss, can be eliminated by an improved etching process.

An excess metal defect is defined as any amount of metal that is not part of the pattern. Any metal in the lighter region of the figure below would be considered excess metal. On the contrary, a void defect is defined as any portion of metal that is missing from the metal pattern. Any hole in the gray region in the figure below would be considered a void. Both types of defects, shown in Figure 20, can cause an entire device to be rejected.

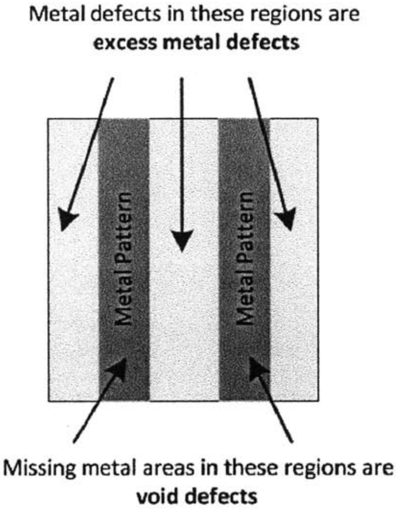

*Figure 20: Visual representation of excess metal*

Preliminary analysis and characterization of excess metal defects showed that there are four primary types of excess metal defects, shown in Figure 21 (reproduction of Figure 4). Further analysis showed that 'speckling' and 'other' defects are likely attributable to a nonuniform photoresist coating. Similarly, droplets could either be photoresist drops that did not dissolve in the solvent correctly or some other drop of contaminant that was able to resist the etchants and protect the metal layers below [1].

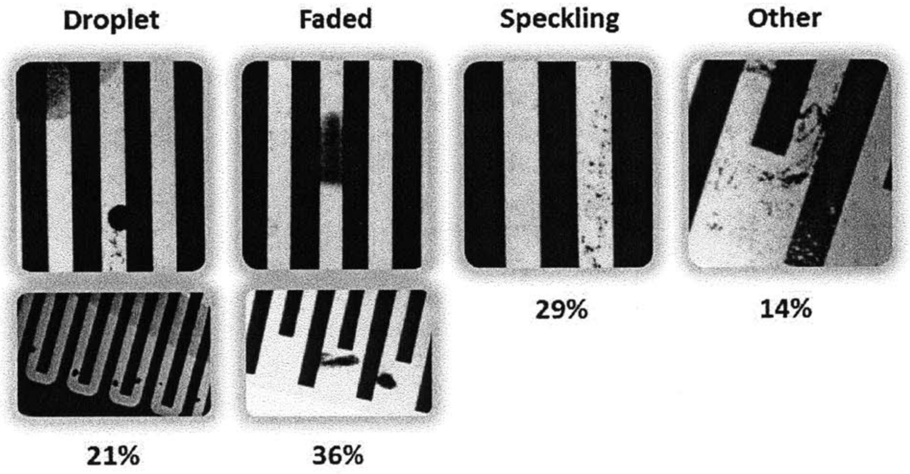

*Figure 21: Types of excess metal defects*

Ten sequential experiments were designed and implemented to explore the source of faded excess metal defects and methods of removal. In the following section, the goals, methodology, and results of each experiment are described in detail.

## 3.1 Problem Classification

In order to classify the problem and define the current process, the current process etch rate and etch uniformity were estimated as metrics with potential for improvement. Figure 22 summarizes the experimental methodology and results required to define the problem.

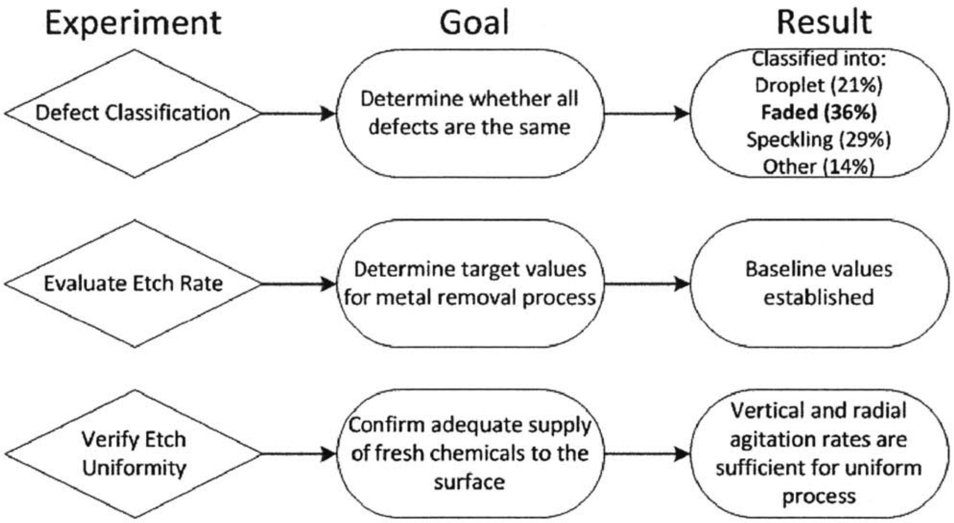

*Figure 22: Problem classification*

### *3.1.1 Etch Rate*

On a smooth surface, it is possible to measure the thickness of a metal layer using a surface profilometer. However, accurate thickness results cannot be established on unpolished PZT due to the high surface roughness of these substrates. Because the etch rate also changes with surface roughness, it was not possible to use this precise equipment with a different surface. Instead, substrates were sputtered with a metal layer of known thickness, and etch time was estimated from a visual analysis.

Nickel Etch Rate

Four substrates were sputtered with .8 microns of Ni on its own. Each substrate was individually immersed into the etch bath, using standard procedures for rotational and vertical chemical agitation. Substrates were examined throughout the etch process, and complete etch time was estimated and recorded in Table 4 with a +/- 3 second uncertainty for each substrate.

*Table 4: Complete etch time for Ni conductive layer*

| Run # | Time to Etch .8 microns |
|---|---|
| 1 | 55 s |
| 2 | 57 s |
| 3 | 55 s |
| 4 | 52 s |

Values were averaged and the results were calculated using (1) as follows:

$$r_{Ni} = \frac{d_{etch}}{t_{etch}} = .0146\ \frac{\mu m}{s}$$

Titanium Tungsten Etch Rate

Four substrates were sputtered with .04 microns of WTi on its own. Etch time was estimated as described above for the nickel substrates and recorded in Table 5.

*Table 5: Complete etch time for WTi barrier layer*

| Run # | Time to Etch .8 microns |
|---|---|
| 1 | 100 s |
| 2 | 106 s |
| 3 | 91 s |
| 4 | 98 s |

WTi etches at a rate of.0004 microns per second, as shown below.

$$r_{WTi} = \frac{d_{etch}}{t_{etch}} = .0004\frac{\mu m}{s}$$

In order to maintain daily etch throughput, it is necessary to maintain or improve these etch rates. Thus, these were used as baseline values for all experimental etchants.

### *3.1.2 Etch Rate Uniformity*

Etch uniformity (2) can provide a metric by which to evaluate the variation in etch rate between several different substrates. A low etch uniformity may indicate that there is insufficient transport within the etch bath and therefore that fresh chemicals are not reaching the surface of each substrate. Etch rate uniformity is provided in Table 6, calculated using (2) using minimum and maximum etch times from Tables 4 and 5 for each metal layer.

*Table 6: Numerical results for etch rate uniformity*

| **Metal** | **Etch Uniformity** |
|---|---|
| **Ni** | 45.9% uniformity |
| **WTi** | 7.61% uniform |

The resulting etch rate uniformity below 50% implies that the supply of chemicals may not be sufficient to reach all substrates. However, because of the margin of error in time measurement (+/- 3 seconds), this data may not be accurate. Further analysis was required to gain a visual understanding of etch uniformity.

For further analysis, 560 substrates were also etched with identical placement orientation into the etch boat. The goal of this experiment was to determine whether defects were concentrated along the depth or radial gradient of the beaker used for etching.

Excess metal and void defects as found from rejected devices were mapped separately according to location and type, as shown below in Figures 23-25. Note that Figure 23 evaluates only the faded excess metal defects, because of their direct relationship to the quality of the etch process.

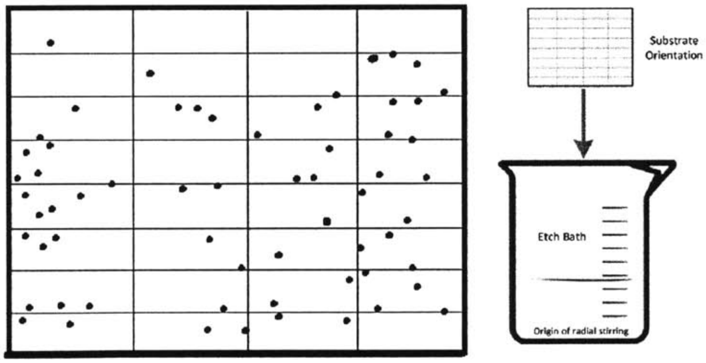

*Figure 23: Location and frequency of faded excess metal defects from 560 substrates*

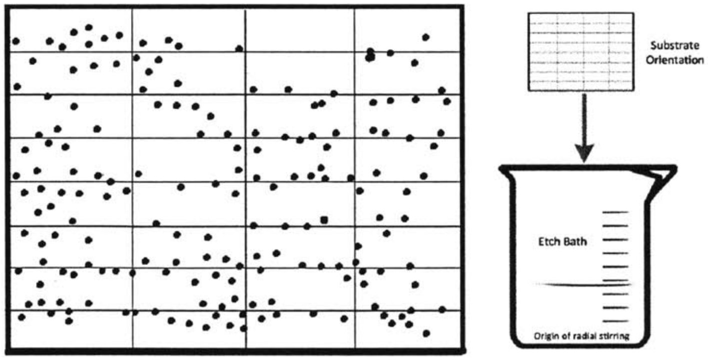

*Figure 24: Location and frequency of all excess metal defects from 560 substrates*

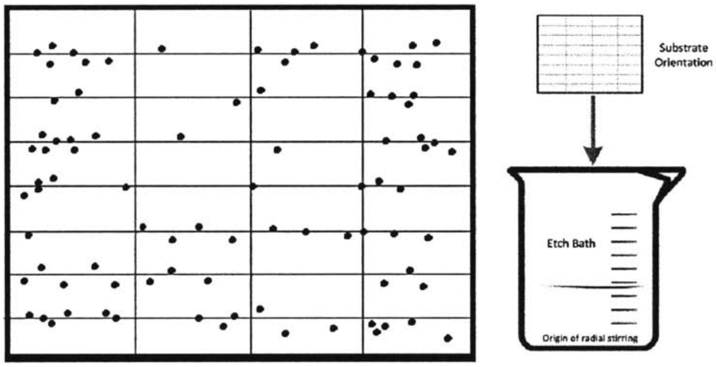

*Figure 25: Location and frequency of void defects from 560 substrates*

Radial chemical flow is applied at the bottom of the beaker in order to supply fresh chemicals the surface of each substrate constantly and evenly. If this flow is insufficient, then a gradient of excess metal defects along the height of the beaker would be found. However, as clear from Figures 24-26, there are no visible quadrants where the frequency of excess metal or void defects is especially concentrated. All locations on the surface appear to have random defect density.

In order to experiment with chemical flow inside the bath, 56 substrates were also etched at half bath capacity, increasing the transport of reactants and products and allowing more space for the surface reaction to occur. Vertical agitation was performed consistently. The yield loss due to excess metal and void defects for these substrates was approximately the same as the average historical yield loss, and it was thus concluded that restricted chemical flow was not the primary cause of excess metal defects.

## 3.2 Defect Causes

Two experiments were performed to identify the cause of faded excess metal defects. First, devices were overetched and examined in order to determine if excess metal defects were pure in composition. An increase in etch time led to a significant increase in the number of voids as the photoresist layer became weaker, and produced only a small reduction in excess metal defects. Thus, it was determined that another layer of unknown composition was covering these defects. Final devices were also etched for extended time in Neutra-clean detergent in order to remove nickel oxide. With a 300% increase in cleaning time, the defects disappeared. These experiments led to the theory that faded excess metal defects are the result of incomplete nickel oxide removal. Figure 26 describes the strategy for these experiments.

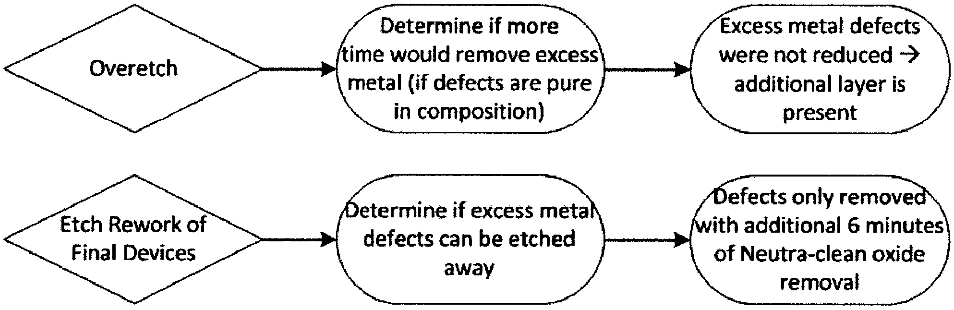

*Figure 26: Experiments performed to identify the root cause of faded excess metal defects*

### 3.2.1 Overetching

To determine whether faded excess metal defects were pure Ni and WTi or included some other contaminant, devices were overetched. Theoretically, pure metal would etch eventually and defects would be removed with extended time, or overetch, in each chemical bath.

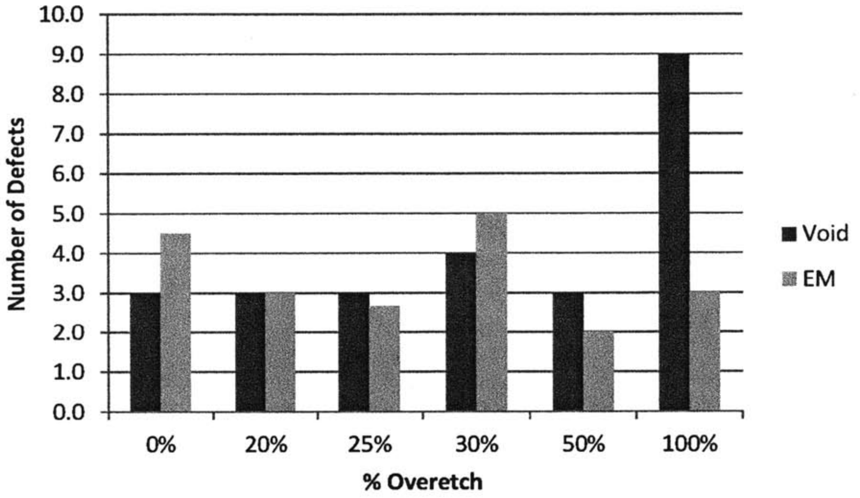

*Figure 27: Summary of overetch experiments*

As shown in Figure 27, with an increase in the time each substrate spent immersed in the etchant, there is a clear increase in the number of voids created due to weakening of the photoresist layer or lifting particles within the layer. However, there is no trend showing a reduction in the number of excess metal defects. Thus, it can be concluded that selectively etching for pure metals to remove excess metal defects is not the ideal solution, and therefore that there is another surface layer that is preventing the pure metals from being removed.

### *3.2.2 Etch Rework of Final Devices*

In order to further evaluate the composition of faded excess metal defects, 20 rejected devices with faded defects, as shown in Figure 28, were selected.

*Figure 28: Example of faded defect*

By placing these devices in the NiO cleanser, Neutra-clean, prior to re-etching, 15 of these defects became faded in nature. To achieve this minimal removal, it was necessary to clean the devices for 300% more time than the process standard. Then, when placed in the nickel etchant followed by the titanium tungsten etchant, the defects vanished almost immediately.

Experimentally etching rejected devices in varying selective etchants to determine their chemical concentration indicated that there was a layer of NiO at the surface of the defect which prevented the metal layers beneath it from etching away. Therefore, it was concluded that the NiO removal process needed to be improved. Because quadrupling the oxide cleansing time prior to etching would severely reduce the process throughput, other chemical combinations were explored. The remainder of this experimental methodology summarizes the analysis and experimentation that took place to optimize NiO removal.

## 3.3 Root Cause Validation

Previous experimentation identified faded defects as layers of NiO that prevent pure Ni and WTi layers from being removed during etching. Two experiments were performed to verify this theory, as introduced in Figure 29.

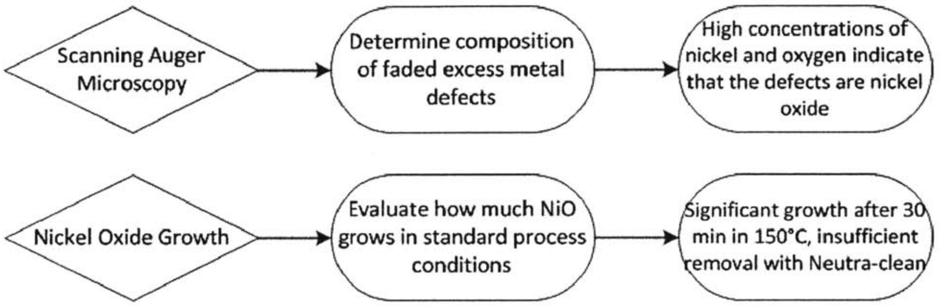

*Figure 29: Experimentation to validate the root cause of excess metal defects*

### *3.3.1 Chemical Analysis: Scanning Auger Microscopy*

To confirm that faded excess metal defects contain a surface layer of NiO, Scanning Auger Microscopy was used to excite the top 10nm of the surface layer and analyze the intensity as a function of kinetic energy. The peaks could then be identified as the natural element that is present. The sample chosen was a faded excess metal defect measured to be 125 microns wide and 200 microns long, as shown in Figure 30.

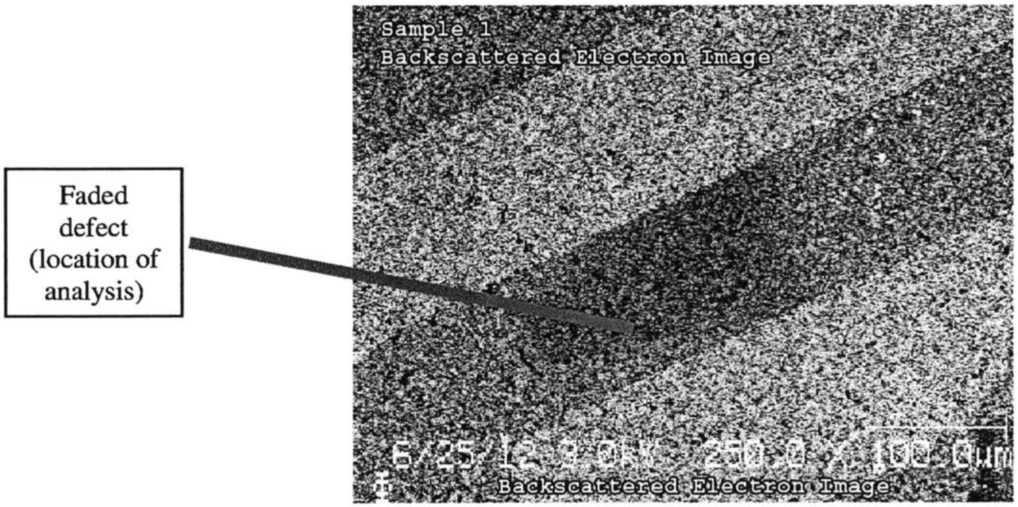

*Figure 30: Backscattered electron image of defect, where lighter regions represent metal and darker regions represent space*

All results for defect and reference regions revealed 40% carbon content at the surface, which could be caused by any environmental conditions or exposure to humans. The initial surface scan produced raised levels of oxygen and nickel, indicating the presence of a nickel oxide layer. Figure 31 shows these results.

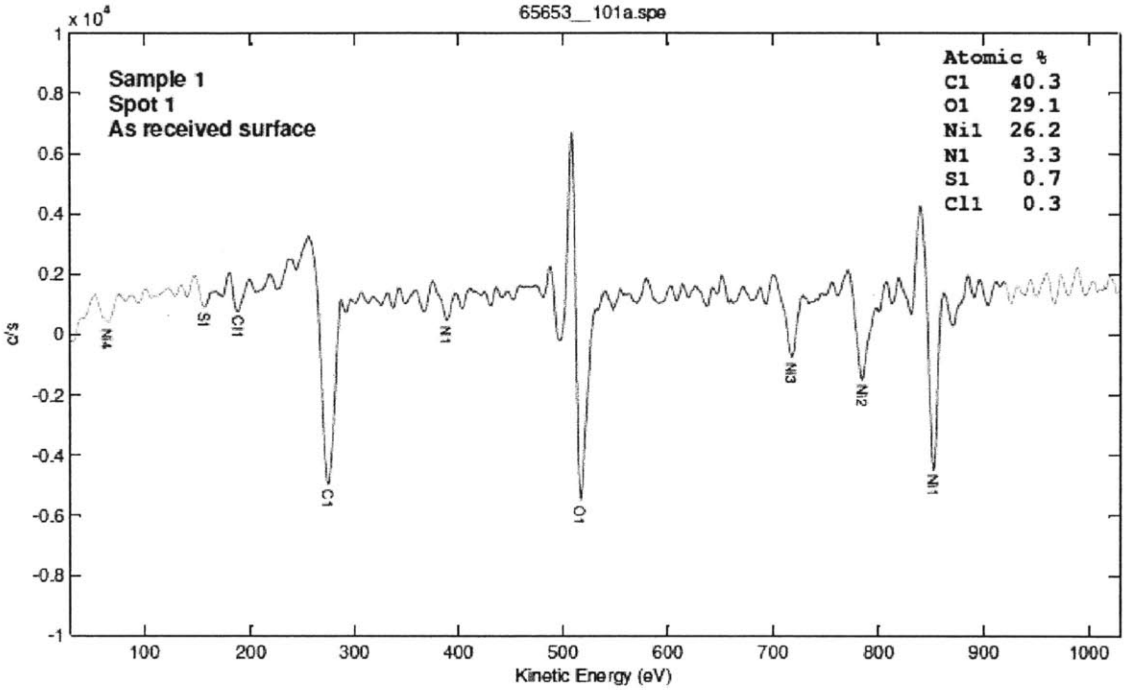

*Figure 31: Chemical analysis of faded excess metal defect*

When the top 500 Angstroms of material were sputtered away and the faded defect was analyzed, the oxygen levels dropped by 17.2%, while nickel levels increased by 31.7%, indicating that at this depth the surface was coated with pure Ni only. Thus, the thickness of the NiO layer is less than 500A. Because commercial oxide removers and etchants will have a baseline etch rate, the etch time to remove NiO can be estimated from this thickness.

Spot 2 in Figure 32 shows the reference space between metallic lines on the device.

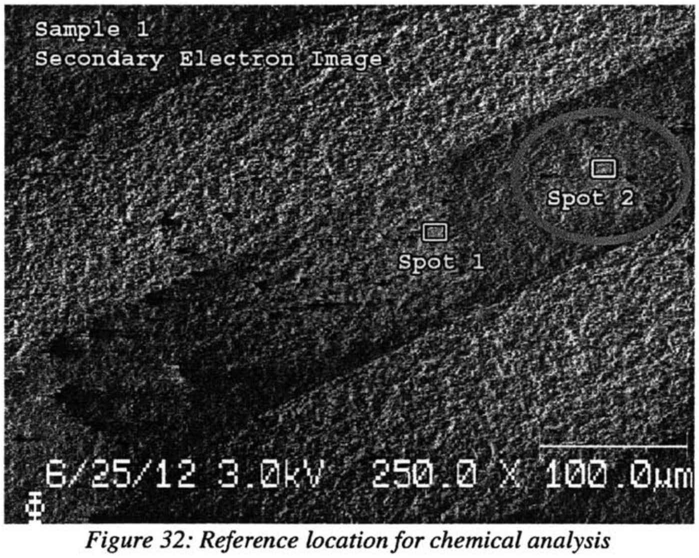

*Figure 32: Reference location for chemical analysis*

Scanning Auger Microscopy performed on the reference region, Spot 2, showed high levels of oxygen, likely due to the presence of oxides in the PZT composition. If all faded excess metal defects are eliminated, analysis of any unpatterned spot on the PZT surface should show similar concentrations of oxygen. Figure 33 provides the intensity curve for Spot 2.

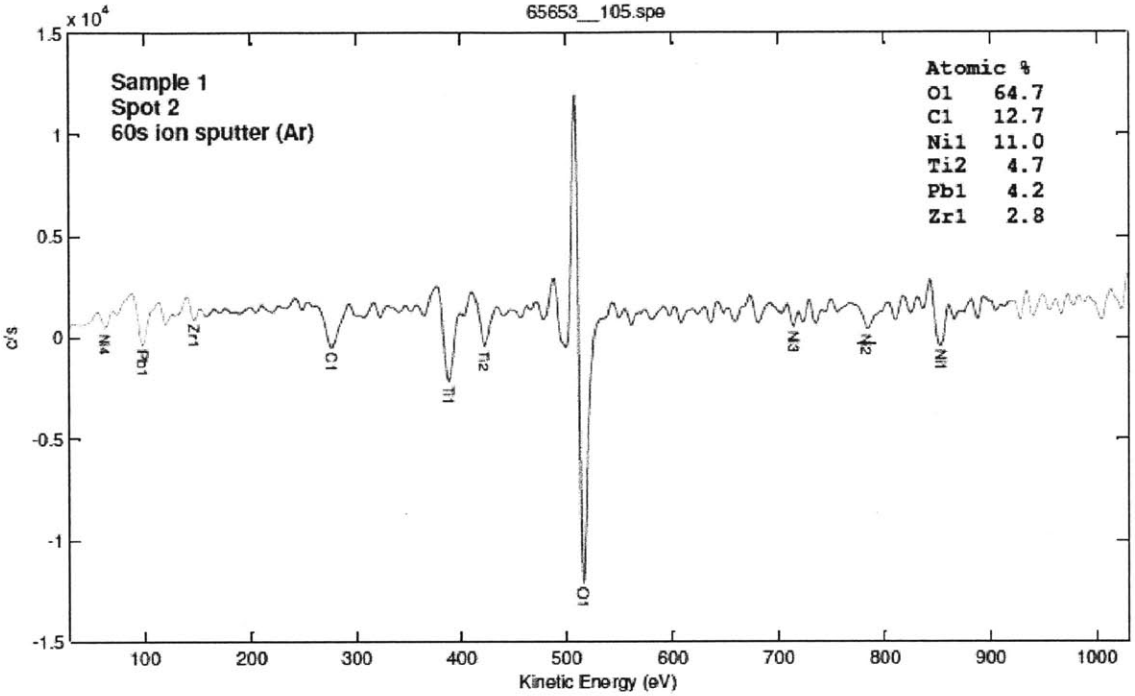

*Figure 33: Chemical analysis results from reference region*

This chemical analysis confirms that faded excess metal defects consist primarily of NiO which prevents Ni and WTi removal during the etching process.

### *3.3.2 Nickel Oxide Growth*

Though research shows that NiO can form even with extended exposure to room temperature surroundings, it is unlikely that the standard process would be unable to remove this amount of oxidation. As a preliminary reference, one polished alumina coupon was held in room temperature conditions for 60 minutes, and etched without Neutra-clean for nickel oxide removal. This substrate showed only small amounts of nickel oxide growth, as shown in Figure 34.

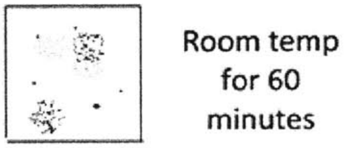

*Figure 34: Room temperature NiO growth on polished alumina surface*

It is hypothesized that the majority of NiO growth occurs during a dehydration bake prior to spraying the substrates with photoresist. At this point in time, the surface of each substrate has already been metalized, and is left standing for a minimum of 60 minutes at 150 °C.

NiO was intentionally grown on 6 polished alumina coupons using the process conditions associated with the dehydration bake before spraycoating. One coupon was removed from the oven every 10 minutes in order to observe the oxide growth. The coupons were then etched without the Neutra-clean oxide removal step, in order to determine the spacial distribution of oxide along the surface. As shown in Figure 35, coupons that were in the oven for more than 30 minutes show significant oxide growth. Coupons showed visible defects that were similar in nature to faded excess metal defects. Additionally, coupons showed large concentrations of dark, circular defect. It is unknown whether these defects represent the droplet defects mentioned in Figure 4.

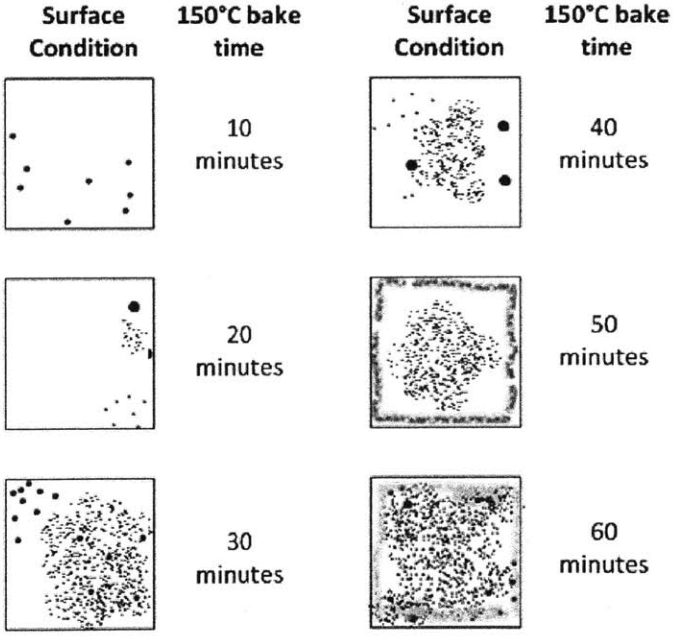

*Figure 35: NiO formation over time as the result of dehydration bake*

In order to determine the ability of Neutra-clean to remove the oxide layers grown at 150°C, two polished alumina coupons were baked to form oxides and then placed through the standard etch process. While the majority of the surface oxide layer was removed, it was clear that isolated defects remained on these surfaces, as shown in Figure 36.

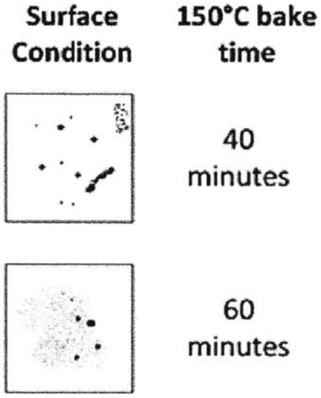

*Figure 36: NiO remaining after standard removal process*

From these results, it can be concluded that there is significant NiO growth during the current manufacturing process of PZT thin films, and that the existing cleaning and oxide removal processes in place are not sufficient to completely remove these defects. It will be necessary to identify an improved process to eliminate excess metal defects due to oxidation.

## 3.4 Identification of Solutions

Available pre-mixed commercial etchants and conventional chemical combinations are predicted to remove both Ni and native NiO layers. Devices were etched using these formulations in order to determine if complete metal and oxide removal was possible. However, results indicated that no commercial etchant used alone would produce the required semi-anisotropic etch profile. It was thus necessary to combine conventional methods with the proprietary etch methods that are currently used. Three experiments were performed to test the validity of proposed solutions, as shown in Figure 37.

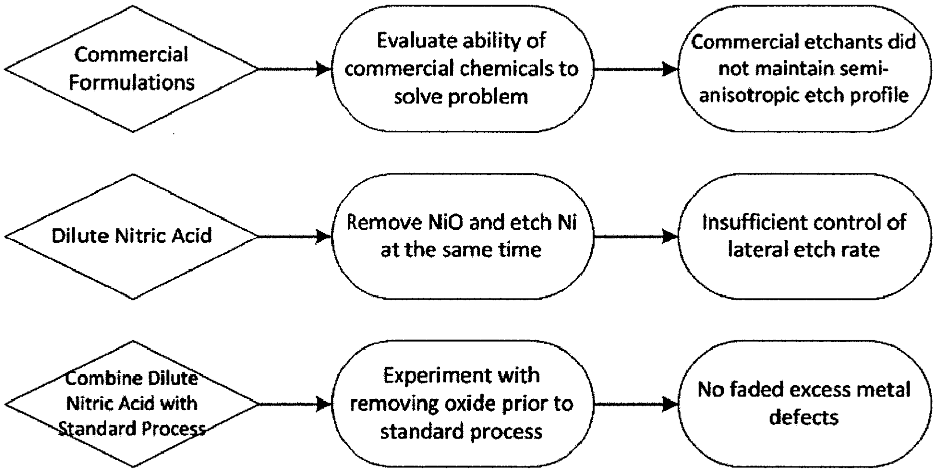

*Figure 37: Experiments performed to test possible solutions*

### *3.4.1 Commercial Formulations*

#### 3.4.1.1 Transene Nickel Etchant TFB

Experiments were first performed with a pre-mixed formulation made by Transene called Nickel Etchant TFB. Based on the predicted etch rate for this chemical, devices were etched at recommended and heated settings [7]. For some tests, the devices were not placed through the standard oxide removal and Ni etch processes in order to evaluate the quality of NiO removal by Transene's chemical only. For the tests that followed, the devices were placed in Neutra-clean cleanser before being etched using Nickel Etchant TFB. Heating the etchant was expected to double the etch rate. The results in Table 7 were obtained:

*Table 7: Results from Transene Nickel Etchant TFB experiment*

| Test # | Time in Neutra-clean (min) | TFB Temperature (°C) | TFB Stir Speed (rpm) | Time in TFB (min) | Time in standard WTi etchant | Results |
|---|---|---|---|---|---|---|
| **1 (proposed)** | 0 | 25 | 350 | 4.5 | 8 | Metal not removed |
| **2** | 3 | 25 | 350 | 4.5 | 5 | Metal not completely removed |
| **3** | 0 | 35 | 350 | 4.5 | 2 | Surface oxide layer remaining |
| **4** | 3 | 35 | 350 | 4.5 | 2 | Surface oxide defects remaining |

A 10°C increase in chemical temperature was expected to double the etch rate, but even with 100% overetch in these conditions, could not completely remove the metal layers. As clear from the results in Table 4, Transene Nickel Etchant TFB is not sufficient to remove the Ni and NiO layers present on these PZT devices.

### 3.4.1.2 Heated Neutra-clean

The current process uses a pre-mixed cleaner made by the Dow® Chemical Company called Neutra-clean, implemented to remove NiO at the surface. At the current temperature of 35 °C, visible oxides are removed but small oxidation defects often remain. These defects restrict the nickel Ni and WTi from being etched at the surface, and correspond to faded excess metal defects at the end of the process.

It is hypothesized that Neutra-clean at a higher temperature may remove even small NiO layers on the PZT devices. However, as the temperature of Neutra-clean is increased, it becomes more difficult to maintain the strength of the photoresist layer and prevent the pattern from being removed. Furthermore, if devices are left in the Neutra-clean bath for too long, the Ni layers will begin to etch away too, resulting in reduced line width due to overetching in the lateral direction.

Devices were placed in a bath of Neutra-clean, heated over a temperature range of 35-55°C. At 35 and 45°C, there was a 50% reduction in the coverage of NiO defects across the smooth coupon surface. After devices were immersed in Neutra-clean for 4 minutes at 55°C, there were less than 2 NiO defects per coupon, but the chemical began to weaken the photoresist and thus cannot be implemented without reducing pattern quality. Table 8 provides these results:

*Table 8: Results from heated Neutra-clean experiment*

| Test # | Neutra-clean Temperature (°C) | Time in Neutra-clean (min) | Time in standard Ni etchant (min) | Time in standard WTi etchant (min) | Results |
|---|---|---|---|---|---|
| 0 (standard) | 25 | 3 | 2 | 2 | Baseline oxidation coverage (100%) |
| 1 | 35 | 3 | 2 | 2 | 50% oxidation coverage |
| 2 | 35 | 4 | 2 | 2 | 50% oxidation coverage |
| 3 | 45 | 3 | 2 | 2 | 50% oxidation coverage |
| 4 | 45 | 4 | 2 | 2 | 50% oxidation coverage |
| 5 | 55 | 3 | 2 | 2 | Infrequent oxidation defects |
| 6 | 55 | 4 | 2 | 2 | Infrequent oxidation defects |

In order to completely remove NiO at the surface using neutral-clean, the chemical detergent must be heated to at least 55°C. Without adding a hardbake step to strengthen the photoresist, Neutra-clean at 55°C will also weaken the photoresist and cause a steep increase in pattern void frequency. Introduction of a hard bake step will reduce throughput and increase the thickness of the surface oxidation layer. Thus, heated Neutra-clean is not the optimal solution for NiO removal.

### *3.4.2 Dilute Nitric Acid*

Dilute nitric acid ($HNO_3$) is a known etchant for rapid and aggressive removal of both NiO and Ni on most surfaces. Experiments were performed to evaluate the effect of dilute $HNO_3$ as a replacement for the currently used Ni etchant.

#### 3.4.2.1 Preliminary Testing

In order to determine a range of experimentation for factorial design, several preliminary experiments were performed. For each chemical combination, four substrates were etched, together intended to estimate the speed and quality of the experimental etch process as described in Table 9. Table 10 shows the parameters and results for these experiments. All experiments maintained the current standard etch process for WTi.

*Table 9: Description of substrates immersed in each etchant*

| # | Description | Reason |
|---|---|---|
| 1 | Sputtered with Ni conductive layer | Determine etch rate of Ni layer |
| 2 | Sprayed with photoresist | Determine if photoresist can withstand etchant |
| 3 | Sputtered with WTi barrier layer and pure Ni conductive layer | Determine if WTi would also dissolve in chemicals |
| 4 | Patterned substrate with all product layers | Estimate line width |

*Table 10: Results from preliminary $HNO_3$ experiments*

| Etchant Name | Composition | Temperature | Ni + NiO Etch Rate | Impact on Photoresist (PR) | Impact on Line Width |
|---|---|---|---|---|---|
| **Concentrated Nitric Acid** | 100% $HNO_3$ | 50℃ | 44.4 A/s | Completely removed | Completely removed |
| **Concentrated Nitric Acid** | 100% $HNO_3$ | 23℃(Room temperature) | 26.7 A/s | Severe necking | Completely removed |
| **Dilute Nitric Acid** | 30% $HNO_3$,<br>70% $H_2O$ | 23℃(Room temperature) | 44.4 A/s | Intact | Reduced line definition |
| **Dilute Nitric Acid** | 30% $HNO_3$,<br>70% $H_2O$ | 45℃ | 66.7 A/s | Minor necking | Reduced line width |
| **Dilute Nitric Acid + Hydrochloric Acid** | 10% HCl,<br>30% $HNO_3$,<br>60% $H_2O$ | 45℃ | 13.3 A/s | Intact | No defined lines |

As Table 10 shows, with a heated bath of concentrated $HNO_3$, both Ni and NiO were completely removed but the photoresist coating was destroyed and thus patterns were also etched away. When the formulation was brought to room temperature, photoresist deterioration was less severe but still did not retain its full strength. However, by diluting the concentrated $HNO_3$and heating it, the Ni etch rate was significantly reduced and the photoresist layer remained intact.

Preliminary analysis also indicated that a solution of dilute $HNO_3$ and hydrochloric acid (HCl) would remove both pure Ni and WTi. However, this solution was unable to break down the oxidation at the surface of the metallic layer, and thus did not quickly remove the metal.

### 3.4.2.2 Design of Experiments for Dilute Nitric Acid:

As shown in Section 3.4.2.1, dilute $HNO_3$ easily breaks down both NiO and pure Ni with heating and agitation. Increasing the temperature, amount of $HNO_3$, and agitation rate will each increase the material removal rate during etching.

In order to optimize the etch rate for these thin films, a set of experiments was performed according to a standard $2^3$ factorial design [15]. The three factors for this experiment were chemical temperature (A), acid concentration (B), and stir speed (C). Each combination was measured with n=1 replicates.

All experiments were performed in a 3500ml Pyrex glass beaker. Increased chemical temperature was achieved with a Cole Parmer® Stabletemp heating plate fitted with a flexible thermocouple probe for accurate measurement and magnetic stirrer for agitation.

Table 11 below presents the etch rate data for this experiment, followed by a graphical representation of the data in Figure 38.

*Table 11: Etch Rate Data for Dilute $HNO_3$ Experiment*

| **Run** | **Combination** | **Factors** | | | **Etch Rate (A/s)** |
|---|---|---|---|---|---|
| | | **A** | **B** | **C** | |
| **1** | (1) | - | - | - | 13.33 |
| **2** | a | + | - | - | 59.26 |
| **3** | b | - | + | - | 25.81 |
| **4** | ab | + | + | - | 106.67 |
| **5** | c | - | - | + | 15.38 |
| **6** | ac | + | - | + | 76.19 |
| **7** | bc | - | + | + | 30.77 |
| **8** | abc | + | + | + | 160.00 |

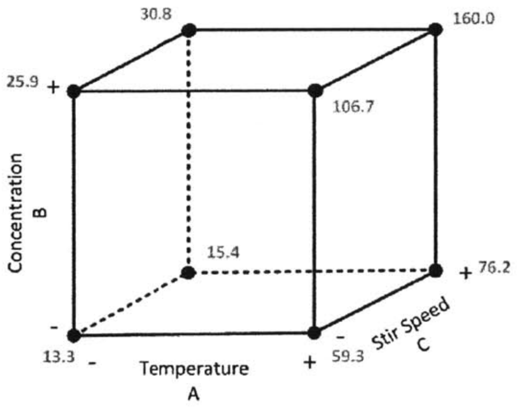

*Figure 38: $2^3$ design for the etch rate with dilute nitric acid experiment (the numbers in green are the single replicate results at each design point)*

Using JMP statistical software, the effects of each factor and interaction were estimated. As shown in Table 12, temperature and concentration (factors A and B) are dominant, and stir speed (factor C) has minimal effect on the etch rate.

*Table 12: Effects for dilute $HNO_3$ design of experiments*

| Term | Effect |
|---|---|
| **A** | 39.6 |
| **B** | 19.9 |
| **AB** | 12.9 |
| **C** | 9.7 |
| **AC** | 7.9 |
| **BC** | 4.9 |
| **ABC** | 4.2 |

To achieve a desired etch rate, it will thus be necessary to primarily control the temperature concentration of the dilute $HNO_3$. To achieve an etch rate of 146 A/s, which is equal to the current Ni etch rate, this model suggests a solution of high temperature and high concentration. However, a solution of heated and highly concentrated $HNO_3$ will break down the photoresist layer immediately, exposing the pattern below and allowing it to be removed. From these results, it is clear that dilute $HNO_3$ alone cannot be used to etch Ni and NiO for these devices.

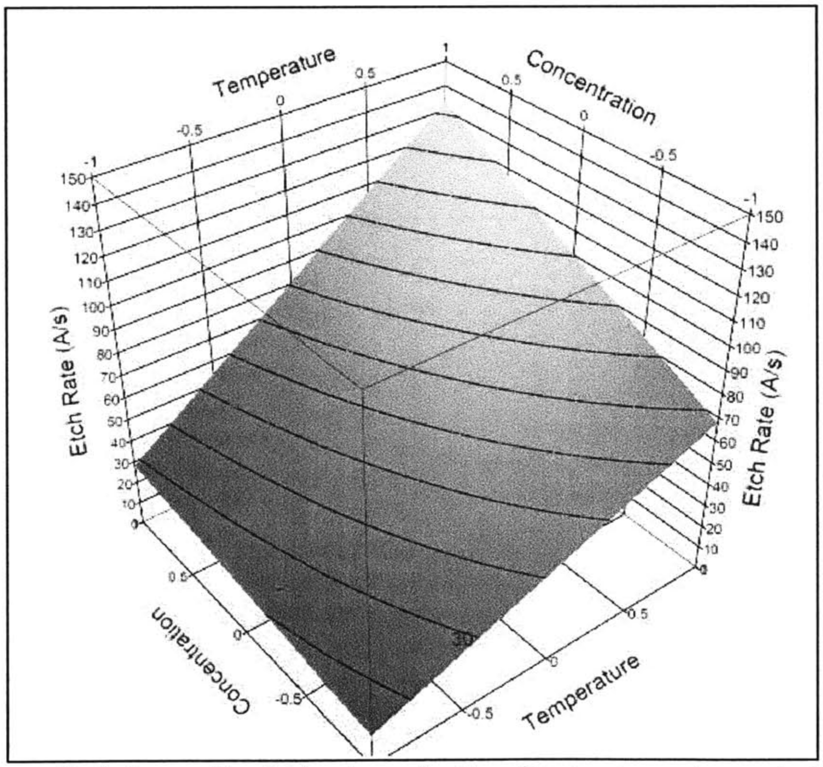

*Figure 39: Surface profile of etch rate as a function of temperature and concentration*

### *3.4.3 Combination of $HNO_3$ and Current Etch Process*

#### 3.4.3.1 Preliminary Testing

The current etch process requires a total of 7 minutes to remove all the metal layers completely. In order to remove NiO by increasing the amount of time immersed in Neutra-clean, it is necessary to increase this process time to 13 minutes. It is necessary to completely remove NiO layers and maintain the semi-anisotropic etch profile achieved with the current etchant used.

Using the results from the two level factorial design indicated that $HNO_3$ has the ability to rapidly remove NiO layers and etch pure Ni layers when heated. Theoretical predictions indicated that the desired etch rate would only be achieved with hot, highly concentrated $HNO_3$. As expected, experimentation showed that the lateral etch rate of this formulation is too high. In fact, even when devices were etched in a solution of 10% $HNO_3$ mixed with deionized water, the pattern lines were no longer straight when the Ni layer was removed completely.

As a result, several substrates were etched with varying fast exposure to dilute $HNO_3$, followed by use of the pre-proven etchant consisting of dilute $H_2SO_4$ and $H_3PO_4$ (verified by the Department of Chemistry at Harvard University [8]). These substrates produced varying results, with four process combinations described in Table 13 that maintain the required line dimension and did not affect the quality of the photoresist layer:

*Table 13: Sequence of etchants with added dilute $HNO_3$ step*

| **Solution #** | **Dilute $HNO_3$ Concentration** | **Dilute $HNO_3$ Temperature (°C) at 350 rpm stir speed** | **Time in Dilute $HNO_3$ (min)** | **Time in Neutra-clean (min)** | **Time in Ni Etchant (min)** | **Time in WTi Etchant (min)** | **Total etch time** |
|---|---|---|---|---|---|---|---|
| 1 | 10% $HNO_3$<br>90% $H_2O$ | 46 | .5 | 0 | 2 | 2 | 4.5 |
| 2 | 10% $HNO_3$<br>90% $H_2O$ | 46 | .5 | 2 | 2 | 2 | 6.5 |
| 3 | 40% $HNO_3$<br>60% $H_2O$ | 42 | .33 | 0 | 2 | 2 | 4.33 |
| 4 | 40% $HNO_3$<br>60% $H_2O$ | 42 | .33 | 1 | 2 | 2 | 5.33 |

All four solutions will reduce the total etch time required for PZT devices at the company, and will thus make contributions to increased production throughput. Solutions 1 and 3 were eliminated because of traces of contaminants at the surface, likely because the cleansing step was not included. Solution 2 was eliminated because of the high process time in comparison to its alternatives.

Solution 4 was used to etch 168 devices, holding all upstream and downstream steps constant with the current manufacturing process. All devices were inspected and no faded excess metal defects were present. Therefore, further experimentation focuses only on Solution 4, proposed for implementation because of its balance between process time and adequate surface cleansing time.

## 3.5 Solution Verification

Research, analysis, and experimental data have confirmed that faded excess metal defects occur as the result of incomplete NiO removal at the surface of devices. Based on exploration of several chemicals and processes, and it was determined that a rapid introduction into dilute $HNO_3$ prior to cleaning and etching PZT substrates would remove these unwanted oxidation defects. As shown in Figure 40, testing was then required to evaluate this method as a feasible process change.

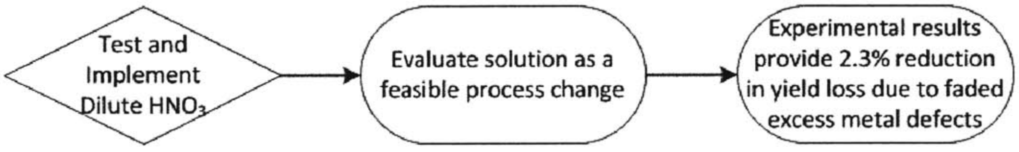

*Figure 40: Methods to verify proposed solution*

The proposed solution for an improved etch process is described in Figure 41:

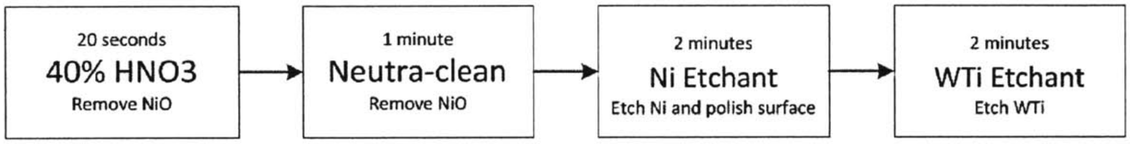

*Figure 41:Proposed etch process to remove NiO defects*

To compare the presence of NiO defects in a single set of process conditions, 196 work-in-progress devices were etched in split lots, where half of the devices were etched with the current process and half were etched with the proposed new process. As shown in Table 14, devices which used only Neutra-clean for oxide removal showed several faded excess metal defects, while devices that were introduced to $HNO_3$ showed none.

*Table 14: Results from split lots to verify solution*

| Process | NiO removal method | Number of Devices | Number of NiO (faded) excess metal defects |
|---|---|---|---|
| **Current** | Neutra-clean | 98 | 9 |
| **Proposed** | $HNO_3$ + Neutra-clean | 98 | 0 |

To test this solution on a large scale, 588 production devices were etched with the proposed process described in Figure 41. Results and careful inspection of rejected devices, categorized in Table 15, indicate that out of 59 total defects, only 6 were due to NiO. This translates to 1% of total yield loss for this set of devices, a value significantly lower than the previously stated 3% yield loss due to NiO defects during defect classification in Section 1.4. All other excess metal defects from this set of devices appear to be due to an uneven photoresist layer.

*Table 15: Results from production testing*

| WO | NiO Excess Metal | Other Excess Metal | Voids | Scratches | Pits |
|---|---|---|---|---|---|
| **1** | 0 | 4 | 2 | 0 | 0 |
| **2** | 0 | 4 | 5 | 7 | 2 |
| **3** | 1 | 3 | 0 | 0 | 0 |
| **4** | 2 | 3 | 3 | 8 | 0 |
| **5** | 3 | 3 | 2 | 1 | 0 |
| **6** | 0 | 1 | 0 | 5 | 0 |

Historical data also indicate that the average work order contains 3-4 void defects. As reported in Table 15, work orders etched with the proposed etch process showed an average of 2 void defects, indicating that using this method would not result in increased yield loss due to void defects.

It is notable that during production testing, 3.5% of devices were rejected due to scratches. Further research and production testing will investigate the cause of these scratches and evaluate any potential correlations to the etch process.

Despite the unexpected scratches during production testing, these results verify the ability of the proposed solution to remove NiO excess metal defects.

# Chapter 4: Conclusions

## 4.1 Yield Improvement

In an ideal process for PZT thin films, substrates are coated with metal and photoresist and then etched to remove remaining metal and preserve the pattern. In practice, due to the intricate nature of these devices, surface contamination can form mid-process, photoresist layers can be sprayed unevenly, and etching requires a delicate balance of etch rate and line width control. At the end of the process, almost 8% of its devices are scrapped due to excess metal defects. In order to reduce the number of scrap devices and improve the manufacturing process quality, it was necessary to identify the root causes of all defects and develop process improvements to eliminate them.

The primary goal of this study was to identify and eliminate faded excess metal defects only, which contribute to approximately 3% of total yield loss. As described in the preceding methodology and results, several sequential experiments were performed in order to classify the defects and their relationship to the etch process, evaluate the root cause of faded excess metal defects, and experiment with solutions to eliminate these defects.

During manufacturing, any steps in which metal layers are exposed to heated surroundings for an extended period, significant oxidation will occur. Experimentation showed that NiO was forming at the surface of substrates. Furthermore, experiments with oxidized substrates showed that the etching process would not break down NiO layers, hindering the quality of these devices. Thus, in order to eliminate excess metal defects caused by incomplete metal removal, it was necessary to revise the etching process. Commercial etchants, aggressive acids, and sequential etch baths were all tested for their ability to quickly remove metal and maintain a semi-anisotropic etch profile.

An optimal solution can be achieved with the combination of heated dilute $HNO_3$, reduced time within the Neutra-clean cleanser, and continuation of the standard Ni and WTi etching processes currently used. With successful implementation of an improved etching process and maintenance of a contaminant free environment, excess metal defects would only exist due to variations in photoresist quality. This improved process is recommended for two reasons:

1. Potential for 3% yield improvement by complete removal of nickel oxide (faded) defects
2. 25% reduction in etch process time upon implementation

## 4.2 Improved Rework Process for PZT Products

Because the thin film manufacturing process requires and maintains a strong in-process inspection procedure, it is also possible to identify excess metal defects and voids immediately after the etch process. One portion of this study identified a process for complete surface layer removal on PZT substrates to rework substrates with visible defects after etched.

Substrates identified with many excess metal defects can be soaked in a heated bath of dilute nitric acid (40% nitric acid and 60% deionized water at 55 °C) to completely remove the NiO and pure Ni surface layers in 3 minutes. With an additional 4 minutes in the standard etchants to ensure complete removal and polishing and a 3.5 minute cleaning process, all metal, photoresist residue, and any other surface contaminants that are not inherent within the material can be removed. No ghost layer will remain on the surface following this process, and all substrates can be reused as raw material. This recommendation is summarized in Figure 42. All recommended process times represent the minimum duration required to completely remove surface layers from PZT substrates.

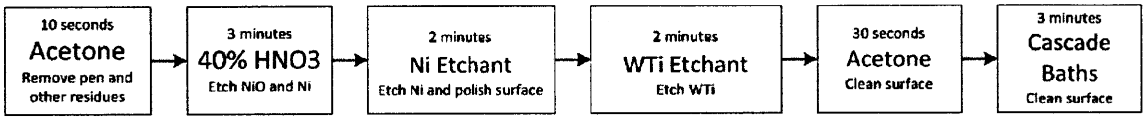

*Figure 42: Minimum process times to rework substrates with high defect density to raw material*

Note that defects identified prior to photoresist removal will require complete photoresist stripping prior to this process. Substrates that are stripped in acetone should be washed thoroughly before immersion into $HNO_3$ in order to avoid safety hazards caused by chemical incompatibilities.

In order to implement this rework process as efficiently as possible, it will be necessary to balance this process. Ideally, substrates should be immersed in each chemical for 2 minutes. Substrates can stay in acetone and water for as long as necessary. Experiments should be performed to increase the concentration or temperature of $HNO_3$ to increase the metal removal rate. An increase in cascade frequency would also allow a shortened cleaning time. The resulting balanced rework process would have a cycle time of 12 minutes.

## 4.3 Future Work

The conclusions of this study show that it is possible to eliminate excess metal defects due to NiO growth at the surface-atmosphere interface with substantial cost savings to the manufacturer. Prior to full scale implementation of an etch process that includes $HNO_3$, a detailed cost analysis should be performed to quantify the savings created with fewer excess metal defects and increased etch throughput. Furthermore, the savings benefit of the etchant used should be considered. $HNO_3$ is commercially available, and can be mixed with deionized water as required within the company facilities. The existing solution, Neutra-clean, is currently purchased as a custom item from its distributor. Using an off-the-shelf etchant will reduce the company's dependency on a single distributor, reduce the cost of materials, and simplify the overall manufacturing process.

Production testing proves the efficacy of nitric acid as an etchant for device components. However, as mentioned in Section 3.5, the control case also exhibited an increase in scratching on several final devices. Preliminary analysis suggests this scratching is the result of handling errors, but it would also be valuable to evaluate any correlation between use of nitric acid and the increased frequency of scratches or microscratches at the surface.

Section 4.2 provides the minimum immersion time required to completely etch and strip substrates for rework. Prior to implementation, it will be beneficial to balance the process times in order to maximize the efficiency of this process

Historical defect classification indicates that excess metal defects result from the combination of the spray-coating and etching process. Once excess metal defects due to insufficient NiO removal are eliminated, further improvements can be made by preventing oxidation upstream in the manufacturing process and assessing the photoresist spraying process. Finally, if possible, further research should be performed to evaluate etchants that can remove NiO, Ni, and WTi simultaneously while maintaining the current unique semi-anisotropic etch profile. Currently, no known etchant has been shown to accomplish this under feasible conditions for the manufacturer. However, if identified, a combined etchant would both reduce oxide growth between etch baths and reduce the number of steps in the manufacturing process.

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