Experimental Electroplating and Material Characterization Using Nanoindentation Techniques

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Abstract – **This thesis focuses on the use of nanoindentation and the characterization of electroplated materials. A team of honors college students will design a test cell for electroplating strips of parts, after which test samples were to be plated. One of the methods which was to be used to test the properties of the plating is nanoindentation, which is be the focus of this thesis. Nanoindentation is a relatively new method, making nanometer sized dents in the surface of the material to test various properties. This thesis explores the history of nanoindentation, as well as its uses and the potential for further use and development of similar techniques.**

I. BACKGROUND

In order to effectively design a physical system, it is important for an engineer to know the physical properties of the material they are using. The general properties for most common materials are readily available, but sometimes an application requires specialized materials or working on very small scales, where materials with known properties suddenly behave very differently. Nanoindentation is a method of determining the mechanical properties of a material, which arose in the late 80's and early 90's in response to the increasing demands of ever-miniaturizing technology [1], [2]. Nanoindentation allows for the properties of materials to be determined on a scale of micro- or nanometers, enabling the analysis of very thin films of materials or of the surface of a material. Since its inception, it has proven to be one of the most rigorous and versatile methods for nanoscale material analysis [1].

The process of nanoindentation is fairly simple. As described in [1], the indentation machine uses a hard tip, or "probe", to prick the material. This probe is typically a three- or four-sided pyramid, although some special applications use tips that are cubic, conic, or even spherical [1]. The tip is extremely small, with a surface area of only a few nanometers or micrometers, but it imparts an enormous amount of pressure onto the surface being indented [1]. In order to be effective the tip must be made from an extremely hard material, typically diamond or tungsten [1] The force that it takes to push the tip into the material is recorded automatically, and this process is then done several times in various locations on the material to create a map of its properties in relation to the position on the sample. From the force data, various mechanical properties of the material can be calculated. For reference, an image of the probe being pressed into a material is shown in figure 1, taken using a scanning electron microscope to capture the process as it occurs [1]. This image shows clearly both the pyramidal shape and the small size of the nanoindentation tip mentioned previously.

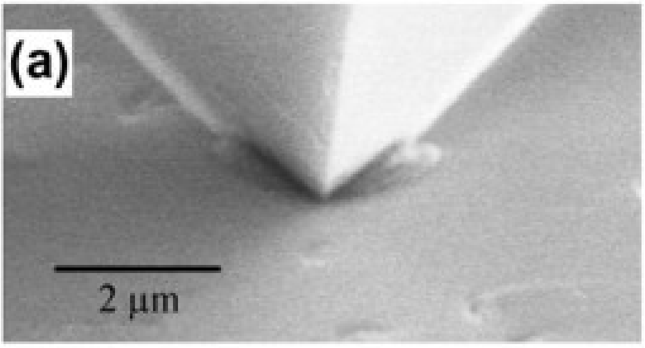

Fig. 1. SEM image of nanoindentation into a thin film on silicon, from [1]

When it was introduced in 1992, nanoindentation was intended to measure only the hardness and the *Young's Modulus*, or elasticity, of a material [1]. In materials science, hardness is a measure of how difficult it is to create a permanent deformation in a material, such as a scratch or a dent, and elasticity is a measure of a material's ability to recover from temporary deformation, like stretching a rubber band. Traditional testing methods can only measure the bulk properties of a material, so nanoindentation was immediately useful in measuring thin films or small amounts which are necessary for more specialized applications [1],[3]. Although the ability to find the hardness and elasticity was useful, research quickly begun on finding more ways to apply the technique and gather more information about how materials behave at nanoscale. Eventually, nanoindentation became the most effective and widely used method for examining nanoscale mechanical properties of materials [1].

One of the first advances in nanoindentation technology was to integrate it with scanning electron microscopes, to allow the observation of the indentation process as it occurs [1]. SEM is the most commonly used method of electron microscopy [1], a group of methods which use electrons instead of visible light to form an image of a surface at a scale of micro- or nanometers. Figure 1 is an example of the sort of image created by this process, although it also allows for not just still images but observing the process in real-time [1]. Developing integrated nanoindentation/SEM machines allowed for the refinement of the theory behind nanoindentation, which still is not fully understood [1], [4-6]. Watching nanoindentation in real-time also allows for more properties of the sample to be studied than just hardness and elasticity. Using these techniques allowed researchers to study more involved things such as how cracks form and spread along the surface of a material [1]. These techniques continue to be useful, more recently being used to aid in understanding the behavior of carbon nanomaterials such as graphene or nanotubes, which are becoming more and more widespread [1].

SEM technology greatly improved the understanding of the nanoindentation process, but it has two major drawbacks, as noted in [1]. The first is that SEM machines can only view the surface of the material, preventing the study of changes within the material as it is deformed. The second is that while SEM machines have a very high resolution, they lack the ability for true nanoscale imagery in real-time, and so cannot be used to study the effect of stress on the scale necessary for some specialized applications. In order to overcome these problems, techniques using a different imaging method were developed. Transmission electron microscopy (TEM) is capable of imaging the changes within the structure of a material at true nanoscale and is the most powerful tool available for the study of materials at near-atomic resolution [1]. An example of TEM imagery is shown below in figure 2.

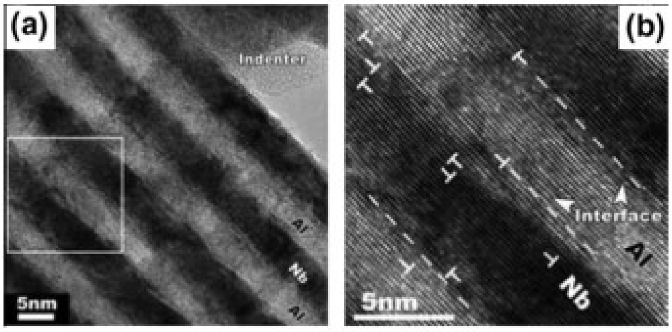

Fig. 2. TEM imagery of Aluminum-Niobium films, from [1]

Figure 2 gives a better sense of the resolution achievable by TEM methods, with (a) showing a cross-section of stacked Aluminum and Niobium films undergoing indentation, and (b) showing the marked section of (a) at a resolution high enough to show the motion of atoms within the material, denoted by the symbols there shown. By integrating nanoindentation and TEM techniques, researchers were able to directly study the correlation between mechanical effects and the actual atomic effects, further refining knowledge of how materials behave at such small scales [1]. However, a great amount of research is required to apply this sort of technique to new materials, as the results are difficult to interpret and require some existing knowledge of how the material will behave in order to give accurate results [1].

Another recent development which has improved the understanding of nanoindentation techniques is in using computer simulation. Given the relatively recent genesis of the technique, it should not be surprising that there were a number of phenomena observed in nanoindentation which went unexplained for some time [5]. Only with the help of advanced computer simulations, capable of simulating the indentation interaction, were some of these phenomena explained, and the majority of this work was done in the past ten years or so [5]. These "atomistic" computer simulations have enabled advancements in the understanding of the mechanisms underlying the nanoindentation technique, as well as yielding new knowledge about how materials behave at small scales [5]. However, there are still many unanswered questions regarding the mechanics which influence nanoindentation testing.

As pointed out in [6], the majority of equations used in calculating material properties from nanoindentation data are empirical. That means that the formulas were created by performing nanoindentation on a material with already known properties, then back-tracking until an equation was found which gave the correct results. The resulting formula then gives accurate results, but only under circumstances resembling those under which it was found. This sort of process is common to many fields and areas of materials science, and typically such equations give accurate results; however, it represents a sizable gap in the understanding of nanoindentation. This becomes particularly problematic when the assumptions underlying such empirical formulas are overlooked, and they are applied to situations in which they should not actually apply [7]. Such misapplications can lead to large errors in the numbers reported, and this is exacerbated by the popularity of the nanoindentation technique and by the difficulty in making direct comparisons with the data given by more traditional methods [7]. This means that although nanoindentation is a promising technique, much of the data reported from studies using the technique is either unsubstantiated or unreliable [7].

Nonetheless, despite the large gaps in understanding of exactly how it works, nanoindentation has become the most popular and fastest-growing method of material characterization for films and small-scale materials [1-8]. The versatility and relative simplicity of the testing method have produced a large amount of research with the purpose of either refining nanoindentation or expanding its possible applications. The more significant refinements to the technique have been discussed above, and the more common applications will be discussed below.

II. COMMON APPLICATIONS

Although the original use of nanoindentation was quite narrow, it proved to be a highly adaptable and versatile method of measuring material properties on a micro- or nanoscale. This capability is increasingly useful, as the push to miniaturize technology necessitates understanding of the way materials behave at ever-reducing scales [8]. It has become quite commonplace as a research method and has greatly increased the understanding of the behavior of small-scale materials. So, although it would be a very difficult and lengthy process to compile an exhaustive list of every application it is currently in use for, it should be sufficient for general understanding to give the most common applications and classes of applications for the technique.

Nanoindentation is most commonly used to find the properties of metals, typically of thin films of them. Nanoindentation allows for controlling the depth of the indentation, allowing the testing of a film only nanometers thick [1], [3]. The general rule of thumb when indenting into a film is to indent no more than one-tenth of the thickness of the film, so that the data is not affected by any material beneath the film [8]. This allows nanoindentation to be used not only for finding the properties of single layers of material but also of layered composite materials or of coatings, such as those shown in figure 2. This ability has contributed significantly to the popularity of nanoindentation techniques, although another significant factor has been the number of different properties which can be observed and calculated from a single test [2]. Some of these properties require specialized methods to record, such as those which require

SEM or TEM machinery as detailed in section I, or a rapidly growing group of measurements: electrical measurements.

Although originally intended to measure only mechanical properties, nanoindentation has recently been repurposed to gather information about the electrical properties of materials as well [1]. This sort of measurement is typically done using a probe which is conductive, typically made from a hard metal such as tungsten or specially treated diamond [1]. By attaching the tip to a current or voltage source, properties such as the conductivity of a material can be measured during the indentation process [1]. As mentioned in [1], this has proved an especially useful capability for the characterization of silicon, a material whose properties have made it arguably on of the most important substances for mankind. But while the electrical and mechanical properties of silicon are well documented, it is not well understood how its electrical properties are affected by the application of force, especially at small scales [1]. Nanoindentation has proved well suited for this sort of study and is being used to study the electromechanical properties of other materials which are becoming more and more prevalent in modern technology, such as graphene and piezoelectric materials [1]. The data gathered on piezoelectric materials this way is particularly valuable, as they are primarily used for the relationship between deformation of the material and voltage across it [1]. In general, the sort of electromechanical data gathered is becoming increasingly important as mechanical and electrical systems become more intertwined.

Another application to which nanoindentation is being applied to with increasing frequency is in measuring how materials behave at high temperatures [1], [4]. Plastic polymers and metals have a number of unique properties at high temperatures which are important to understand for forming operations which take place at high temperatures. By heating up the sample before nanoindentation, the material can be studied while it is near its melting point and as it cools, giving information about how these materials cool and solidify, and different factors which affect those processes [1]. A general diagram of a high temperature nanoindentation setup, as shown in [1], can be seen below in figure 3.

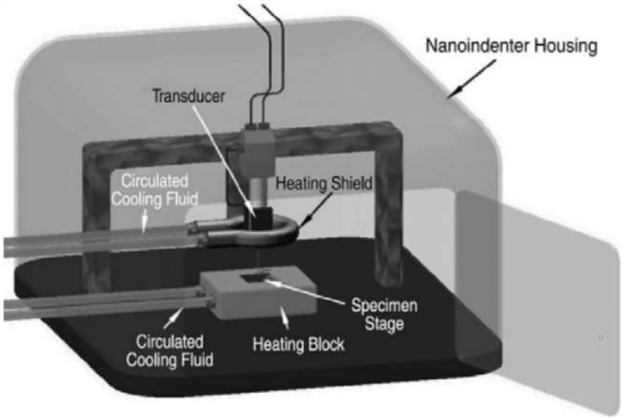

Fig. 3. General diagram of instrumentation for high temperature nanoindentation [1]

In the diagram, the transducer is the means of measuring the force with which the indenter presses into the sample. It is important to note that, as shown in the diagram, the high temperature of the sample specimen requires the more delicate parts of the nanoindentation instrument to be shielded and cooled, to prevent it from being destroyed [1]. This sort of high temperature application still has many difficulties to work out, such as the sample oxidizing or the temperature changing while the measurement is taking place, before it can be fully reliable but promises to provide valuable information for the field of materials engineering [1], [4].

Another field of materials science which nanoindentation is being applied to is in the design of plastics, or polymers. Nanoindentation is most commonly used to analyze metals because they have properties which make them easier to study with the method [1], but it is being used more and more on polymers and polymer composite materials as they only continue to become more prevalent [7]. Polymer-based composite materials, or materials created by mixing a polymer with other materials, are of particular interest for this analysis as their properties are not always well understood [7]. Composites containing carbon nanotubes and graphene are among the most studied of these, as there is an increasing focus being put on carbon nanomaterials in general [1], [7]. However, polymers and polymer composites present unique challenges to use in nanoindentation testing. Because polymers are softer than metals, special tips have to be used to get accurate data, typically spherical or conical in shape [1]. Additionally, when testing composites the orientations of the materials mixed into the base materials must be determined and accounted for, as they produce directional dependence in the properties of the material [7]. The small amount of available data itself is also a hindrance, as it makes corroborating findings extremely difficult [7]. Nonetheless, nanoindentation continues to be used for polymers and polymer composites, and refinements will continue to improve its applicability thereto.

There is of course overlap between these testing applications and methods. As mentioned above, polymers are often measured at high temperatures, as they exhibit unique and complex behaviors at elevated temperatures [1]. Understanding these behaviors is critical for high temperature forming operations done with polymers, such as injection molding. Measuring the electrical properties of a material could be done at elevated temperatures and combining this with the real-time imagery provided by SEM or TEM machinery helps to study the change in electrical properties caused by mechanical stress.

Nanoindentation has proven to one of the most versatile measurement techniques for determining the properties of materials at a micro- and nanoscale. There are many more ways in which it has been used not mentioned in this thesis, and more applications are continually being researched. To create an exhaustive list is beyond the scope of this thesis, but the above brief overview of its common uses should give an idea of the sort of application it is used for and of the potential for new uses of the technique, such as the one which will be proposed later in this thesis.

III. NANOINDENTATION AND ELECTROPLATING

Electroplating, also sometimes called electrodeposition, is the process of creating a metal coating on a part by means of a process involving electricity. There are many different methods of electroplating, but the one which is referenced in this thesis involves using a chemical bath to facilitate the transfer of metal ions. The metal to be plated is connected to the negative terminal of a current or voltage source and submerged in a chemical specific to the plating process [9]. The donor metal, which will end up plating the part, is connected to the positive terminal and placed in the plating chemicals [9]. A general schematic for the electroplating process can be seen in figure 4, taken from [9].

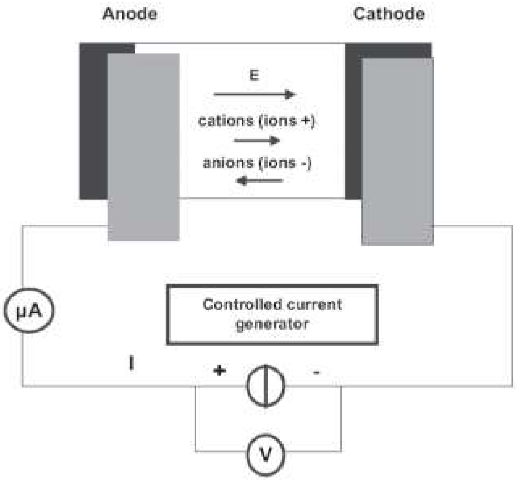

Fig. 4. General schematic for the electroplating process, from [9]

The donor metal is referred to as the anode, as shown in figure 4, and the part to be plated is referred to as the cathode. The anode dissolves positively charged particles in the chemical solution, and these particles are attracted to the oppositely charged cathode [9]. In this way, multiple layers of metals can be deposited onto the surface of a part so long as it is conductive. The general purpose of this process is to modify the cosmetic, electrical, or mechanical properties of a part to make them more desirable for the application. For example, copper has many properties which make it desirable for use in electrical applications, but it is a relatively soft and weak metal. If a copper part required better mechanical properties, such as increased surface hardness or more resistance to bending, it could be coated with metals which possess such properties. The resulting part would be a composite material, with properties influenced by both the bulk metal and of the metals plated onto the surface.

A group of engineering senior design students at Oakland University were tasked by an automotive company with designing a semi-automatic electroplating process, which would be used for research and development purposes. The process had to allow a strip of copper parts, attached to a feed reel, to be plated continuously and end on a product reel. The company also wanted work to be done on characterization of potential materials for use in electroplating their parts, and for validation to be done on parts plated by the student-designed electroplating process. This sort of in-depth material characterization is beyond the capacity of the typical automotive manufacturer due to the specialized equipment and knowledge required, and typically plated parts are otherwise tested using less refined methods, which could only test the performance of the part as a whole. Nanoindentation testing could be used to further the company's understanding of how various materials behave when used as plating, as well as how the properties of the part as a whole change when new materials are added.

Oakland University has in its possession a NanoTest™ nanoindentation machine, which can be used for such material characterization. A diagram of this system can be seen below, in figure 5.

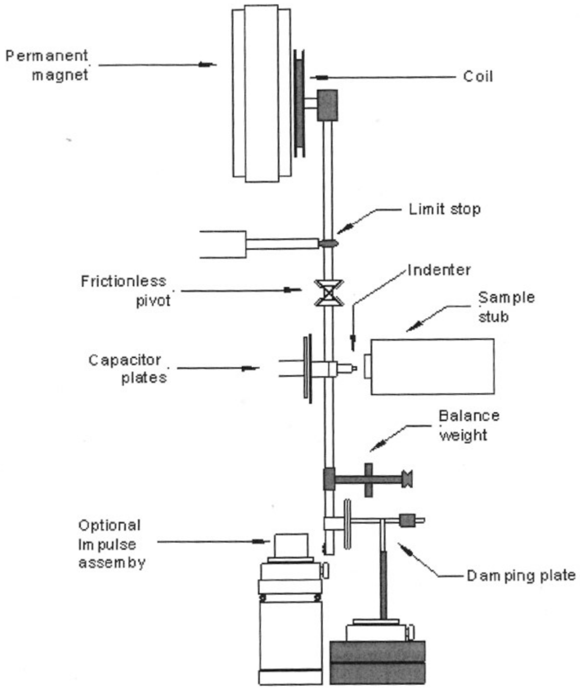

Fig. 4. Diagram of the NanoTest™ nanoindentation system, from the equipment manual [10]

The basic principles which the instrument uses are relatively simple. The indenter, in this case a pyramid shaped diamond probe, is hung in front of the sample on a theoretically frictionless pivot, as shown in figure 5. The balance weight ensures that the arm remains balanced about the pivot, so that the only force required to swing the arm should be the force that is required to push the indenter into the sample material. The force for the indentation process is provided by means of the coil at the upper end of the indenter arm, which forms an electromagnet. When indentation is to occur, electrical current is fed through the coil so that it becomes attracted to the permanent magnet near it, and it swings the bottom end of the indenter arm around the pivot so that it comes into contact with the sample. The damping plate at the bottom reduces vibration which would interfere with the data gathered, and the limit stop restricts the range of motion in the indenter arm so that it does not move too far. In order to precisely measure the depth of indentation, a parallel plate capacitor is used [10]. The capacitance of the plates changes in relation to the distance between them, so by measuring the capacitance during the indentation test the distance which the indenter pushes into the sample material can be calculated with a resolution of better than one nanometer [10]. This high resolution is necessary for the analysis of extremely thin films, as the maximum distance into a film which should be indented is one-tenth the total thickness of the film [8]. For a better idea of the nanoindentation setup located at Oakland University, pictures of the actual setup can be seen below in figures 6-8.

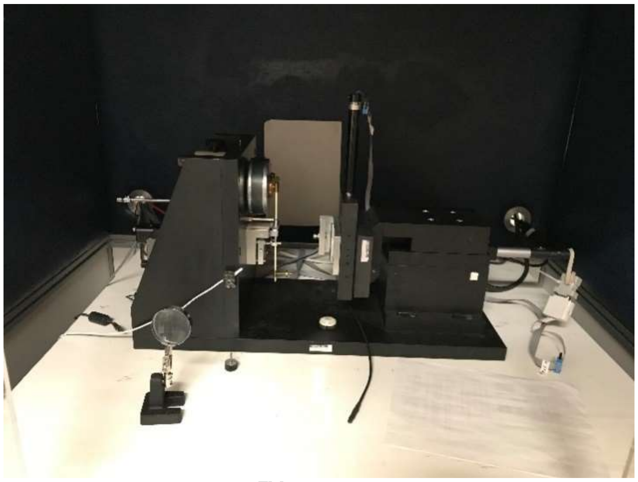

Fig. 6. NanoTest^{TM} Nanoindentation platform

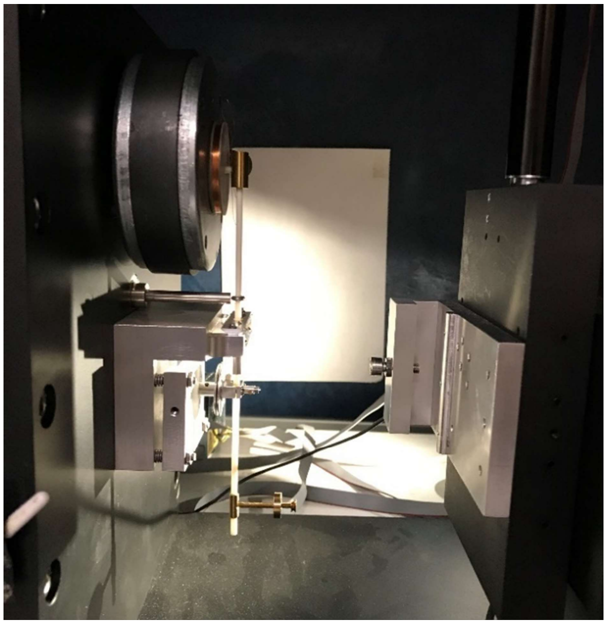

Fig. 7. Closeup of indenter arm, with tip, coil, balance weight, sample holder, and capacitor plates visible

Fig. 8. Computer setup to control the nanoindentation machine

Figure 6 shows the actual indentation machine, located inside of an enclosed testing unit to protect the delicately calibrated machinery. The right side of the nanoindentation platform as shown in figures 6 and 7 is taken up by the sample holder and three direct current motors, which allow for adjustment in the x, y, and z directions independently. Figure 7 gives a closer view of the indenter arm shown in the schematic from figure 6, although the damping plate and Im pulse assembly shown on the schematic are not present on Oakland University's indentation machine. The machine is controlled by software running on the computer shown in figure 8, which also automatically records the data during the indentation process.

Due to unforeseeable circumstances, no testing could be done on the materials which were to be plated as part of the senior design project, so instead this will be a discussion of how the analysis could have been carried out using the instrumentation available at Oakland University. In order for the measurements to be accurate, the sample must be carefully prepared, and a lengthy procedure must be followed to run the machine. The full, detailed procedure is located in the equipment manual kept in the lab with the indentation machine, but an overview of the process should give a sufficient idea of the requirements.

In order for the measurements to be accurate, the surface of the sample to be tested must be as flat and smooth as possible [6]. To achieve this, the materials lab at Oakland uses an ion mill, a device somewhat similar to a sandblaster on a very small scale. The ion mill accelerates very small particles towards the sample, cutting into the surface and leaving an almost completely smooth surface. The ion mill can also be used to cut through a part, leaving a cross-section to be tested. By cutting across an electroplated part, the individual layers of material are exposed so that their properties can be determined separately. Samples are placed in mounts which will allow them to be placed in the nanoindentation machine, depending on their size. Very small testing samples are typically sunken into a block of clear resin, to make handling them easier.

Once the test samples are mounted and then milled, they can be placed into a special plate, which screws into the sample holder shown in figures 6 and 7. Once the sample is mounted, the computer has to be turned on and the sample must be positioned using the motors on the sample holder of the nanoindentation machine so that the tip is positioned over the area which is to be indented. In the lab at Oakland, this is done with the aid of a magnifying glass, although more precise positioning could be achieved by an indenter with an integrated Scanning Electron Microscopy (SEM) machine or other such equipment capable of high-intensity magnification. Before each indentation test, the nanoindentation machine must be run through a series of calibrations to ensure that it is functioning properly and that the measurements taken will be accurate. Indentation is typically done at a minimum of three different locations on one sample, both to ensure the accuracy of results and to account for small differences in the material properties which occur in relation to the position in the sample. The maximum depth for indentation is also set, to allow for the testing of thin films and surface properties of materials. As data could not be gathered from an actual electroplated sample, figure 9 below shows an example the raw data received from a nanoindentation test, using the raw data received from making three indentations into the same material.

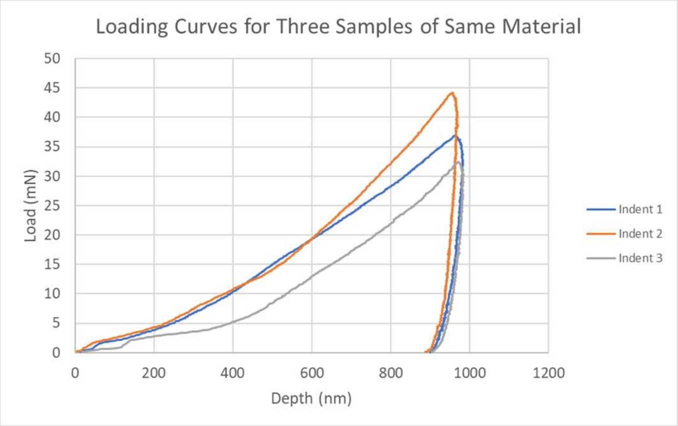

Fig. 9. Graph of raw data received from three indentations into samples composed of the same material

Although figure 9 shows clearly that there are differences in the properties of the material at the indentation site, the data in this form is not as useful as it could be. The software is capable of generating a table of properties calculated using the raw data from the indentation test. Some of these calculated properties can be seen below, in table I.

TABLE I
SAMPLE CALCULATED MATERIAL PROPERTIES

Indent	Max. Depth (nm)	Max. Load (mN)	Hardness (GPa)	Er (GPa)
1	983.991996	36.89079	1.650867	179.137272
2	970.360028	44.185146	2.008059	276.187389
3	984.9137	32.458318	1.433126	193.406415
Mean	979.755241	37.844751	1.697351	216.243692
Errors	8.149535	5.921331	0.290272	52.400737

“Indent” in the table refers to the order in which the three indentations were performed, and correlates to the numbering of the curves in figure 9. As mentioned in section I, hardness is a measure of how difficult it is to permanently deform a material, and “Er” represents the elastic modulus, a measure of the material’s ability to recover from temporary deformation. These are the primary mechanical properties necessary for mechanical design, but more data could be gathered from the samples.

As mentioned earlier, nanoindentation can be improved by coupling it with SEM technology. The Oakland University materials lab also contains a combination SEM and energy-dispersive spectroscopy (EDS) machine, and it was planned to use this to gain more information from the nanoindentation of electroplated materials. EDS allows for the elemental composition of a sample to be analyzed by bombarding it with x-rays and recording the wavelengths of resulting radiation. The SEM/EDS machine in the Oakland lab is shown below in figure 10.

Fig. 10. Combined SEM/EDS machine at Oakland University

Although this machine does not allow for the real-time viewing of the nanoindentation process as mentioned in section I, examining the samples after nanoindentation would yield additional information. The SEM machine could be used to verify the depth of the indentation made and observe the effect of mechanical stress on the plated layers. Unfortunately, this could not be done as no nanoindentation testing was done on plated samples, but there was EDS testing done. Figure 11, shown below, shows an EDS analysis of a part with a single electroplated part, cut so that a cross-section is visible.

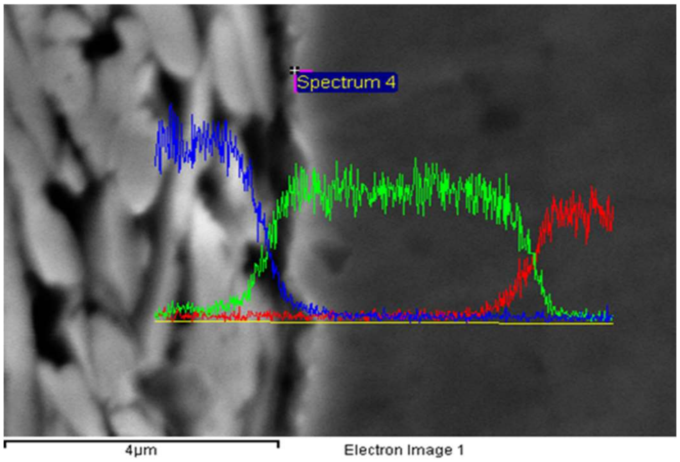

Fig. 11. EDS analysis of a cross section of an electroplated sample

Although EDS analysis is not the focus of this thesis, figure 11 does give a better sense of the scale of the electroplated layers which would be analyzed using nanoindentation. The graph overlaid on the SEM image shows the presence of three different elements in the sample, with red being copper, green being the metal used to plate the part, and blue representing silver. The silver is not part of the plating but is present on the sample because a silver paste was used to adhere it to a mount for SEM testing. The graph shows more clearly the differentiation between the bulk copper of the part and the thin layer of metal which was used to plate it. Unfortunately, the thinness of this plated layer presents an issue for the actual analysis to be carried out.

The method of analysis proposed for this thesis is to cut a plated sample into a cross-section, such as the one shown in figure 11, and nanoindentation would allow the properties of both the individual layers and of the bulk material to be analyzed. However, this analysis is currently only theoretical, for reasons beyond the unpredictable closing of Oakland University's campus during the project. Although such an analysis would be greatly beneficial to the company which sponsored the project, it proved to be beyond the capabilities of both the company and the facilities at Oakland. As can be seen in figure 11, the thickness of a plated layer is only a few micrometers, making it very difficult to indent directly into it. Technically speaking, the indenter at Oakland is capable of indenting into a layer of that size but positioning the indenter with such precision is impossible with the current instrumentation. Doing so would require a nanoindentation machine with an integrated SEM machine, or similar equipment which would allow the indenter to be positioned under high magnification.

Nanoindentation shows great promise for use, in combination with scanning electron microscopy technology, to improve the production of electroplated parts. Materials behave differently on the scale of a thin film or plating, and so it can be difficult to predict how plating a part will affect its properties. Nanoindentation and SEM machines are beyond the reach and knowledge of most companies which do commercial electroplating, so this sort of analysis is not widely done in the industry. Cutting a cross-section of a plated part and then indenting each layer of the electroplating individually would not only give information about how the properties of the plating materials change when used in thin films, but also about the suitability of the plated part for the application it was designed for. This, in turn, could lead to the development of more effective plating materials and combinations of materials, increasing the efficiency of development for parts used in various applications, from automotive to electrical to manufacturing. However, at present this analysis is not possible given the instrumentation at Oakland University. Proper analysis of this sort would require a nanoindentation machine able to be more precisely controlled, to allow for individual layers of thicknesses of a few nano- or micrometers to be analyzed. Other, more specialized, equipment could also be added which would allow for more in-depth analysis to be carried out by nanoindentation. For example, certain equipment mentioned in [1] would allow for not only mechanical analysis of parts but also electrical analysis, broadening the range of information which could be gathered from a single test. Given the proven versatility of nanoindentation techniques, there is no doubt that it will be put to use in an application similar, if not identical, to this sometime in the near future.

IV. SOURCES

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