PLASMA ASHING AS A FIRE INVESTIGATIVE TOOL

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ABSTRACT

One of the difficulties that has faced engineers who examine electrical or mechanical items and / or devices after a fire is that of cleaning the item. The key adage in cleaning is essentially a medical command – *primum non nocere,* or "do no harm." The cleaning technique will preferably cause no damage to the artefact being examined. Successful cleaning allows for both microscopic, visual, and SEM / EDX analysis.

In a fire, it is not uncommon for fire artefacts (wires, as an example) to require cleaning. Historical cleaning techniques have relied upon ultrasonic cleaning as a means for debris removal. Ultrasonic cleaning makes use of mechanical (sonic) energy to cause debris to dislodge from artefacts. How successful this technique is depends (in part) upon the energy imparted, the solvent used, and the interface between the wire and the debris. In the case of partially pyrolyzed PVC insulation, there are conditions that occur (depending upon the state or extent of pyrolysis) where no amount of mechanical agitation will remove the fire debris.

Oxides can be removed from wires by the use of surfactants or cleaners, some of which can have an etching effect on the metal. Treatments such as *Alconox* or *Simple Green* sometimes work sufficiently, while a more aggressive oxide remover *(Branson OR)* relies on citric acid to help clean the wires. With more aggressive reagents, the user runs the risk of etching the metal and ruining the surface finish.

The writers describe a technique for removing fire debris from metal objects (wire, CSST) for use in removing fire debris. The technique is referred to as *plasma ashing*. In plasma ashing, a vacuum is created around the artefact, and a carrier gas is introduced (such as O2). An RF field (13.56 MHz) is applied, and the oxygen takes on a monatomic state. Essentially, a *plasma is* created, and the monatomic O is free to react with organics associated with the fire debris. This process is also referred to as a *glow discharge*. The end result is that organics are removed from the artefact, and the ashing takes place at low temperatures – sufficiently low such that grain structure of the metal is not changed. This technique is essentially what is used in one of the manufacturing steps for making integrated circuits (ICs). As such, it imparts sufficiently low energy such that crystalline semiconductor structures are not damaged.

We compare and contrast plasma ashing with other modalities of cleaning. More particularly, we note (through visual microscopy) the efficacy of ashing and ultrasonic cleaning, as well as material removal rates. We show that despite its relative expensive capital costs, ashing represents a cleaning technique that does what other modalities fail to do – consistent removal of organic debris with no damage to the underlying substrate.

HISTORY

Plasma ashing is a subset of a process called *plasma etching.* A *plasma* is essentially the 4th state of matter. We are all familiar with the concepts of solid, liquid, and gas. This 4th state of matter is present when a gas (or air) is ionized. The plasma has resistivity (conductance) characteristics that are similar to those of metals. On earth, we are familiar with a plasma in the terms of an arc or lightning. Plasma discharges also form the basis for neon sign illumination. What is not realized by many is that a plasma forms the majority of the universe, in that a plasma is present at every star. As with gas, a plasma occupies the shape of a volume that contains it.

Unlike diatomic or noble gasses, an abundance of charge carriers causes the plasma to become an electrical conductor. Ergo, plasma will react to the presence of E-M fields.

Practically speaking, a plasma is a partially ionized gas that has an equal number of negative and positive charges, and different (and constantly changing) number of unionized molecules that are in a neutral state.

To make a plasma in a lab setting, one takes a gas and reduces its pressure. This is done in a controlled vacuum chamber. After pressure is reduced to about 80 millitorr, a gas (in our case, oxygen) is bled into the chamber. Whenever a gas is subjected to RF (Radio Frequency) a *glow discharge* is produced. The glow that is produced occurs as optical emissions are generated by electronically excited particles. Many of the emissions are in the UV region. The colors produced are based on the gasses being disassociated – N2 produces a pink glow, O2 is light purple, and argon is blue. The ionization of an argon atom takes place as shown:

-Ar -> Ar+ + e

When the argon atom is exposed to the RF, this atom becomes disassociated and a bound electron is ejected.

A second and related process which occurs is that of *disassociation.* With disassociation, diatomic gas molecules (as an example) can be split. Obviously, this will not work with monatomic gasses such as argon. There may or may not be ionization that results from disassociation. See the following:

e- CF4 -> 2e + CF3+ + F (Disassociative Ionization)

e + CF4 -> + CF3 + F (Disassociation)

The end result of all this, as it pertains to fire investigations, is that diatomic oxygen is converted into monatomic oxygen. This monatomic oxygen is extremely reactive. When applied to cleaning fire damaged specimens, a specimen is placed into a vacuum chamber. The air is pumped out, down to a pressure of about 80 millitorr. Oxygen is introduced, and an RF field is applied by means of an oscillator (13.56 MHz), with a wattage of ~ 100 watts. The RF and low pressure cause disassociation of the 02 molecules. This monatomic oxygen is then free to react with cellulostic debris, The continuing vacuum exhausts the byproducts, which principally are CO and CO2. This process of combining monatomic O with the carbon fire debris is called *plasma ashing.*

Plasma ashing is merely an extension of *plasma etching*, which has been used for at least 30 years in semiconductor manufacturing. In the semiconductor industry, it is necessary to remove the debris of a type of chemical called *photo resist.* This removal must be done without damaging the delicate crystal lattices structure of the various p-n junctions. The etching process similarly cannot cause damage to the lattices by raising temperatures substantively. Given that semiconductors can be damaged at 350 to 400 deg C, we know that plasma ashing will be extremely safe to use with the removal of fire debris from common metals found at a fire scene – such as zinc, brass, aluminum, steel, stainless steel, and copper.

RESEARCH

Research was conducted by the authors on copper wire samples. We used the following equipment:

Plasma Etcher	PE XL50-HF
Ultrasonic Cleaner	Branson 3510
Microscope	LeicaMZ7.5

Wire Samples

We exposed #12 AWG solid copper wire to flames from a propane torch, to a point where the majority of the insulation (PVC) was pyrolyzed, but also at a point where the copper conductor could not be clearly examined. The wire samples with pyrolyzed insulation were then cut into samples of each about 1" in length. Two samples were used for each ultrasonic technique, and one for the plasma cleaning. The following cleaning techniques were used:

Ultrasonic bath with water
Ultrasonic bath with isopropyl
Ultrasonic bath with acetone
Ultrasonic bath with Alconox
Ultrasonic bath with Branson OR (6 %)
Plasma Ashing

For the ultrasonic bath, the temperature was set at 123 deg F, and clean time was 60 minutes. The plasma ashing was carried out in 2 hours, with an O2 flow rate of 15 mL / minute, and pressure of 80 millitorr.

RESULTS

We present the results pictorially, with both before and after shots. Some may view this as a 'nonscientific' or 'relative' method, but in fact, that is the nature of the research – can we improve our ability to examine copper wires optically while not damaging the underlying copper.

Water

Before **After**

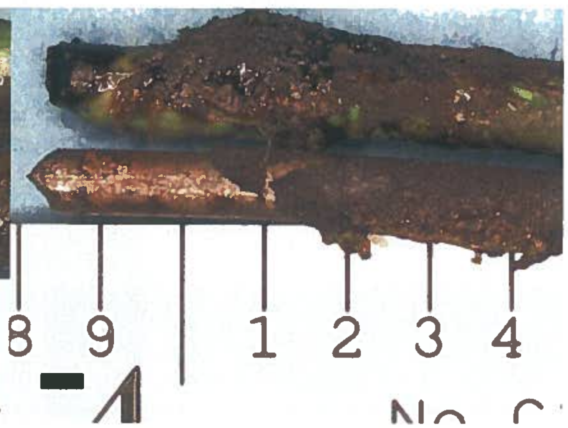
Isopropyl

Before

After

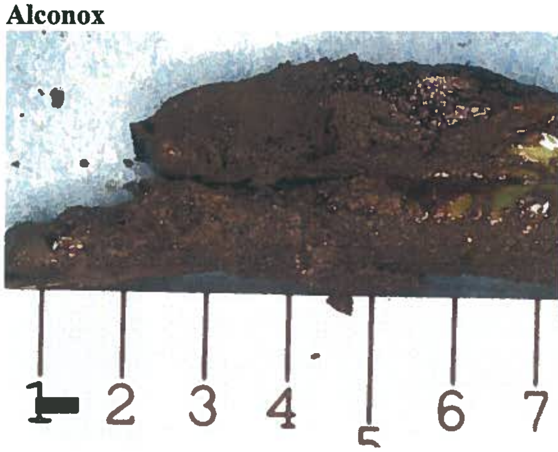
Acetone

Before



After

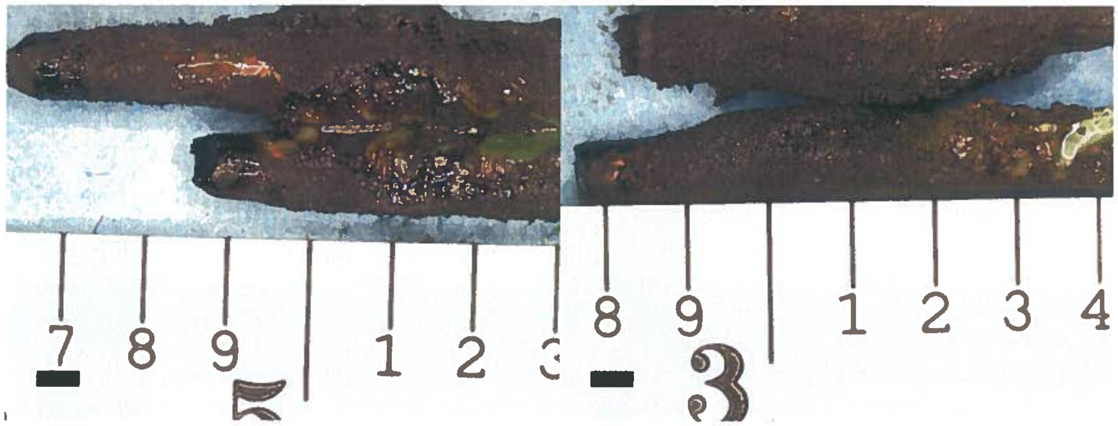
Alconox



Before

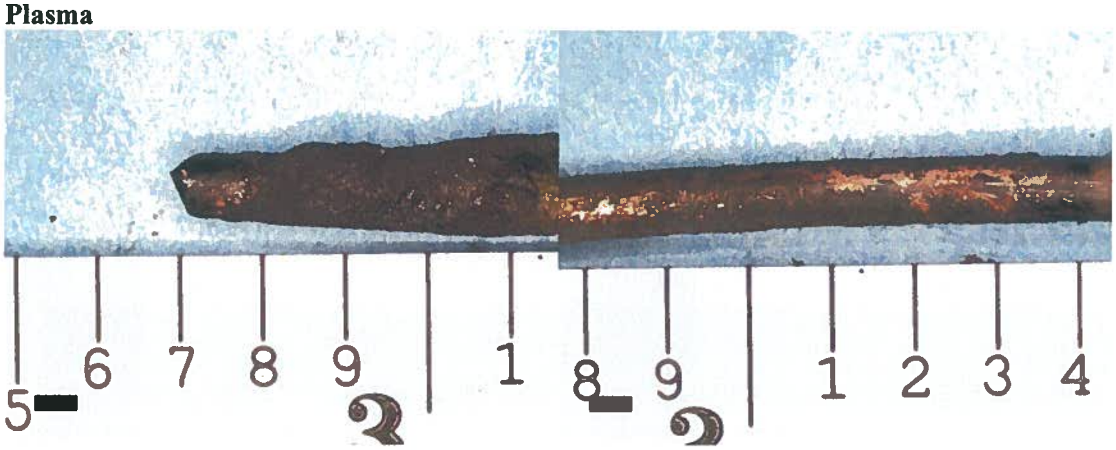
After

Branson OR



Before **After**

Plasma



Before **After**

What is clear is that the ultrasonic modalities do a poor job of removing the remains of partially pyrolyzed PVC insulation. We did note that the agitation and handling, in some cases, brought about flaking of some of the mechanically unstable remains. But in no case did we feel that the ultrasonic cleaning was instrumental in causing a degradation or out and out removal of the pyrolyzed insulation.

The plasma cleaning, however, did present a better alternative to ultrasonic techniques. It was able to remove substantial amounts of the carbonaceous products. As such, it is a viable (in some ways) tool for use in Failure Analysis, FA. This is the result we expected, in that the available monatomic oxygen was able to react with the carbon products that were part of the charred PVC. Moreover, Branson OR (as an example) has in its composition citric acid. There is no known reaction between citric acid and PVC. It is the ability of the monatomic O to react in the plasma that gives plasma cleaning it powerful abilities.

DISCUSSION

What we have demonstrated is that plasma ashing represents a viable tool for use in Failure Analysis, FA, particularly in analyzing fire debris. By way of knowledge of the plasma etching process (to remove photo resist from silicon wafers), we know that the temperature does not exceed that necessary to destroy Si junctions. In principle the basic upper temperature limit of each semiconductor material is determined by its *bandgap energy.* A rule-of-thumb is that the maximum temperature (in K) is *approximately* 500 times the bandgap energy in eV. For Si (band gap energy = 1.17 eV), this rule yields $T_{max} \sim 500 \times 1.17 =$ 558 deg K = 312 deg C. This temperature (312 deg C) is also under the annealing temperature of copper, which is 371 deg C. In that aluminum traces and Si junctions are not affected during plasma etching of photo resist, we felt that the plasma process would also have use with FA *vis a vis* ashing of the fire debris that had cellulose / carbon compositions. The low temperatures involved will thus be harmless to copper and aluminum, as well as Stainless Steel 304 (CSST composition) and the bronze and brass families.

What we did not anticipate was the inefficiency of the technique. The plasma asher requires power for both the vacuum and the RF field. By way of comparison, a 7 watt soldering iron, if applied to a several inch length of jacketed wiring for a few minutes, will literally melt / pyrolyze all of the Poly Vinyl Chloride (PVC) jacketing, albeit with temperatures in the range off 800 deg F. Plasma ashing, by the same token, represents a process does not alter the metal, and unlike the solvents used with ultrasonic baths, removed much of the carbonaceous products present on the copper wires.

SUMMATION

Presented here is a novel technique for bringing about the nondestructive removal of carbon products from wiring for purposes of FA. The technique, plasma ashing, was borrowed from the semiconductor industry. In that it can be used to clean silicon wafers, there is no danger in causing changes to the metallic structures associated with wiring or CSST. It is an expensive technique (in terms of capital), and it does require advanced planning to use – for a joint lab exam, it might take several hours to clean wires suitably. The cleaning process generates a plasma, and monatomic oxygen makes this O available to combine with carbon products to form CO or CO2.

ABOUT THE AUTHORS

Mark Goodson received a BSEE from Texas A&M in 1979, and is licensed to practice engineering in numerous states. After engineering school, he attended UT Southwestern (Dallas) in a forensic medicine track. He was the first PE to serve on the State of Texas Electrical Board. From 1989 to 1991, he served as a Court Special Master. He is the PE selected to sit on the Texas State Fire Marshal Science Advisory Workgroup, SAW. He is a member of the Editorial Review Board for the Fire & Arson Investigator
Mr. Goodson is the principal in the firm Goodson Engineering of Denton, Texas. He holds 3 patents on fire safety, and has 4 more pending. He has published 35 peer reviewed technical articles, with 30 of them dealing with fire science. He has published in the Fire & Arson Investigator, Journal of Forensic Sciences, American Journal of Forensic Pathology, and the Forensic Sciences Gazette. Mr. Goodson serves as a consultant to many Medical Examiners' Offices in Texas.

Lee Green is a Mechanical Engineer who is licensed to practice engineering in ten states. His BSME degree was received from Oklahoma State University and has completed two master's degrees; one is Systems Engineering and one in Engineering Management, from Southern Methodist University. He currently works for Goodson Engineering performing failure analysis. Lee has performed root cause failure analysis on many items large and small from wind turbines and vehicles, to residential appliances and plumbing systems. The majority of failures have resulted in personal injury, water losses or even fires. His previous employment was at Peterbilt in which he designed front engine accessory drive componentry.

Michael Shuttlesworth is a Mechanical Engineer who is licensed to practice engineering. His BSME degree was received from Oklahoma Christian University. He works for Goodson Engineering performing failure analysis on residential appliances and plumbing systems. His specialty is in Mechanical and Electrical failure analysis instrumentation.