



Extramural Research

Final Report: Precision Cleaning/Submicron Level Cleaning With Liquid/Supercritical CO2 Technology

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EPA Contract Number: 68D99050

Title: Precision Cleaning/Submicron Level Cleaning With Liquid/Supercritical CO2 Technology

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Small Business: GT Equipment Technologies Inc.

EPA Contact:

Phase: I

Project Period: September 1, 1999 through March 1, 2000

Project Amount: \$70,000

RFA: Small Business Innovation Research (SBIR) - Phase I (1999)

Research Category: SBIR - Pollution Prevention, Pollution Prevention/Sustainable Development

Description:

This project was aimed to investigate the feasibility of photoresist stripping and the removal of sub-micron particles from semiconductor wafer surfaces. Prior to this investigation, the Los Alamos National Laboratory (LANL) had demonstrated that Super Critical Carbon Dioxide (SCCO2) technology could be used for photoresist stripping in the manufacturing of IC's. Photoresist is a polymer covering the surface of a semiconductor and is used as a mask to protect specific areas of the wafer surface from not being processed in subsequent steps. After the process, the photoresist has to be removed entirely from the surface again. GTi manufactures a patented SCCO2 drying system that is used to release structures of Micro Electro-Mechanical Systems (MEMS) devices which is an offshoot of semiconductor industry. In MEMS devices tiny mechanically moving elements are combined with electronic circuitry on a silicon wafer. The moving elements are etched out of the silicon during the same manufacturing procedure that is applied to make the electronic circuitry. Accelerometers as sensors for air bag deployment or ABS braking systems are such commercially used MEMS devices. The GTi SCCO2 cleaner/dryer prevents the moving elements to stick to the wafer surface during drying and enables the manufacturer to design devices, which in their properties are only limited by the physics that is involved, but not by shortcomings of the cleaning and drying process. The preliminary results from LANL using SCCO2 to strip photoresist, showed the capability of this new technology to replace conventional processes, and GTi's success with SCCO2 drying suggests a leverage effect of the SCCO2 technology on the design of future devices. Although successfully applied to two specific processes (photoresist stripping and drying) there was further R&D work needed in order to extend the SCCO2 technology to general wafer cleaning and photoresist removal.

In a semiconductor production line there are always problems associated with capturing particulates that contaminate the surface of a wafer limiting the production yield. There are various wet methods currently practiced, which are capable of reducing small sized particulates (diameters of around 1 µm or smaller, so-called sub-micron particulates). One method is the wafer scrubber, which uses a rotating brush combined with a flow of deionized water. The second is to use a high-pressure water cleaning apparatuses, which use a high-pressure water jet that is directed across the wafer surface. All of these methods rely on the effect, that particles are flushed off the wafer surface by means of high velocity water flow. In both cases the wafer spins fast around its vertical axis. These methods are very common in production lines. There are other methods like carbon dioxide snow-jet, but are of minor importance.

There is a trend in the manufacture of semiconductor devices to reduce the dimensions of their structures. The smaller the critical dimensions are, the more prominent the particulate contamination problem becomes. It is apparent that a cleaning device, which not only would strip photoresist or clean a wafer but also could reduce particulates would bear severe advantages over conventional devices. The above-mentioned machines for example, are separate units, which consume additional expensive clean room space.

An understanding of this process is crucial to the long-term goal of replacing conventional wet processing systems in a semiconductor production line by Liquid Carbon Dioxide (LCO2) and SCCO2 cleaners.

The obvious advantages of particulate removal using CO2 are:

- switching between LCO2 and SCCO2 to take advantage of the different physical properties of both states,
- density adjustments in SCCO2 is possible by control of temperature and pressure,
- dissolving power of CO2 to remove organic particulates,
- dissolving power of CO2 to weaken interactions between surface and particulates containing organic material,
- easy drying of the wafer surface (CO2 is a gas under normal conditions) avoiding recontamination,
- Ultra-purification of CO2 possible in the supercritical state providing the cleanest agent possible,
- can be applied after photoresist stripping in the same chamber.

This investigation consists of Four Technical Objectives:

Task 1: Experimental Validation of Feasibility of Cleaning and Particulate Removal Process

Task 2: Modeling of Flow Inside a Pressure Chamber

Task 3: Analysis of Expected Results

Task 4: Preliminary Design for the Next Generation Wet-Station.

Summary/Accomplishments (Outputs/Outcomes):

As a result of this investigation, we are able to show that it is possible to remove photoresist from silicon wafers using SCCO2 and a co-solvent. We have learned in that order to do this successfully requires a chamber geometry that will allow a turbulent yet uniform flow throughout the chamber. Our existing lab setup helped in providing basic information that would be very useful in designing and manufacturing of a system during phase II of the project.

Sub-micron particle removal was accomplished using liquid CO2 to flush particles from the wafer surface. This, like photoresist stripping, requires a chamber geometry

that will allow a turbulent yet uniform flow throughout the chamber. Our current hardware, in particular the chamber, has an inefficient geometry for the application. This chamber has a flow that is very laminar. As a result, we noticed dead zones on either side of centerline of chamber. This resulted in stripping or cleaning of wafers only at the center of the chamber. However the particles were removed across the centerline because of existing pressure vessel geometry. Once a new system is designed and fabricated in phase II, we will be able to work on process parameters to optimize processing conditions.

The co-solvent doesn't mix well with CO2 under static conditions. It was nearly impossible for us to dissolve the co-solvent in the reservoir bottles without agitation. In order to get SCCO2 and co-solvent to mix, we had to inject the co-solvent into a flowing stream of SCCO2 as it entered the chamber.

There were also many peripheral findings that will be useful for the design of the next generation wet-station. Such findings include issues with chemical/material compatibility. For instance, the Teflon seats in the ball valves undergo a rapid decompression. Even though the Teflon seats are chemically resistive to the co-solvent and to CO2 at low pressures, high pressure CO2 in its liquid and supercritical state migrates into the seat material. When there is a large differential pressure, the escaping CO2 destroys the seats and allows for the valve to leak.

Conclusions:

We have shown it is feasible to remove hard-baked photoresist and sub-micron particulates from silicon wafers with our experimental setup. We need to do a detailed engineering design and manufacturing of prototype system that will be fabricated in phase II of the project. The setbacks and limitation identified with the first system needs to be overcome. The prototype will take the footprint of a SEMI MESC component with a 6-cluster geometry. The chamber will have geometry such that there is a uniform and turbulent flow throughout the chamber. A closed loop delivery/recovery system will be integrated into the tool. This delivery system will consist of an injection pump, metering valve, and CO2 supply (from recovery system). The recovery system will be capable of reclaiming CO2 as well as separating co-solvent from waste. There will be some means of endpoint detection so that we know when the photoresist is fully stripped. The system will have to generate a minimal number of particles for cleanroom acceptance. Once the prototype system is developed, we will optimize process conditions and take steps towards commercialization in phase III.

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Type	Citation	Project	Document Sources
Journal Article	Critical Point Drying and Cleaning for MEMS Technology, I. Jafri, H. Busta, and S. Walsh; Micromachining and Microfabrication SPIE, Vol.3880 (September 1999).	68D99050 (Final)	not available

Supplemental Keywords:

Supercritical CO2, Micro-Electro-Mechanical Systems, MEMS, Micro-Fabrication, Wafer Cleaning, Photoresist Stripping, Sub-Micron Particulate Removal, Plasma Ashing., Water, Scientific Discipline, Sustainable Industry/Business, Waste, Technology for Sustainable Environment, Engineering, Chemistry, & Physics, Chemistry, cleaner production/pollution prevention, Hazardous, New/Innovative technologies, process modification, semiconductor manufacturing, clean technology, CO2 - based systems, clean technologies, wafer cleaning, particulates, semiconductor industry, wet cleaning alternatives, microelectromechanical systems (MEMS), innovative technology, hazardous chemicals, supercritical carbon dioxide (SCCO2) technology, innovative technologies, pollution prevention

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