초임계 이산화탄소를 이용한 상용 웨이퍼 포토레지스트 세정 공정 개발

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Process Development of Photoresist Removal from Commercial Silicon Wafers Using Supercritical Carbon Dioxide

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Abstract

In recent years, a significant research attention has been placed on the alternative replacement of DI water and toxic chemicals in wet cleaning and photoresist removal in semiconductor industry by the environmentally-benign supercritical carbon dioxide-based gas phase solvent. However, due to the unfavorable property such as low density and low solubility of resist substances at supercritical state, it is not yet practically implemented. During the last several years, the present authors also have been focused their attention on the searching appropriate property modifiers and subsequently the development of dry cleaning processes. In this article, some significant results obtained to date such as modifiers, process conditions on the removal of resist from commercial grade patterned wafers is discussed.

Introduction

Due to the increased environmental regulations on the use and release of toxic chemicals and costs of ultrapure water (UPW) and solvent use in various cleaning and photoresist removal units, the semiconductor industry is in the urgent state of searching alternative tools of abating chemical and water use in the wafer fabrication facilities. For example in a single fabrication line, there are about thirty to forty subunits of wet cleaning stations and they have to use tremendous amount of UPW and toxic chemicals such as sulfuric acid, hydrofluoric acid, ammonium hydroxide and so on. Thus, it is imperative to find an alternative environmentally-benign cleaning technology. Among various new concepts, the dry cleaning without using UPW and with greener solvents such as carbon dioxide is gaining prominence.

The high compressibility of supercritical carbon dioxide and the dependence of solubility or organic substances, transport and other properties in density allow solvent quality to be widely varied by simple pressure control without introducing a phase interface. Temperature must simultaneously be optimized for solvating power since the volatility of the solute increases with increased temperature. The low surface tension of the supercritical phase, another distinct advantage for manufacturing sub-micron features, allows complete wetting of complex substrates with intricate geometry. These attractive capabilities of supercritical carbon dioxide have been the impetus for many recent innovations[1-4].

Years ago, the industry-academic collaboration research group wherein the present authors affiliated are working for the explore the possible replacement of wet cleaning station in wafer fabrication station by a dry cleaning with the greener solvent carbon dioxide by the addition of solubility enhancing modifiers. They also developed alpha-type cleaning units and exclusively devoted themselves for the practical development of the envisaged technology. This article reports some of results obtained to date

Uncovered Process Difficulty of Carbon Dioxide in Wafer Cleaning

In early 1990s, the R&D team at the LANL in the States proudly announced their technological breakthrough of dry cleaning by adopting carbon dioxide at supercritical state. It becomes a corner stone to resurge of boosting the replacing of wet cleaning in garment dry cleaning and semiconductor sectors and other related industry. However, even when we limited ourselves on the replacement of wet cleaning in semiconductor industry such as wafer cleaning and photoresist removal, there was not yet fully commercialized due to the intrinsic deficiency of the physical property of carbon dioxide. For example, even in the supercritical state with high pressure in order to maintain high density, the adjusted density of supercritical carbon dioxide is far lower than that of water at ambient pressure and this low density of carbon dioxide make it difficult to solubilize the photoresist polymer materials. Especially, in between the fabrication steps, the resist polymer is supposed to degraded due to the plasma etching and the substances produce several unknown degraded substances.

To enhance the limited solubility of resist substances in supercritical carbon dioxide, it is usual to adopt various property modifiers. However, the modifiers known to date are the high molecular weight organic substances with high normal boiling point. Thus, when the dry process is depressurized, the modifiers is apt to condensed to the wafer surface. These phenomenon also hinders the practical implementation of the supercritical cleaning process. Also, the supercritical cleaning unit is operated at extremely high pressure and frequent pressurization and depressurization operations are required and this requirement make it difficult to follow the throughput of the existing fab line.

Despite of these underlying drawbacks of the supercritical cleaning process, it becomes imperative to practically implement to fab line due to the overwhelming positive effect of the greener solvent in the immediate years to come. Present work is tried to solve these problems with the commercialization of the technology in mind and discussed in the present article.

Why the Supercritical Greener Solvent in Wafer Cleaning

In addition to the stringent environmental problems related to the wet cleaning in semiconductor industry, there are several practical reasons why the wet cleaning has to replace by nonaqueous cleaning methods. In the first place, the wafer and chip makers strive themselves to produce highly integrated chip. Thus the distance between the circuit become nanoscale and the aspect ratio become severe. For example, to clean up any resist residue in trench, the water is penetrate into the bottom of the trench, solubilize and diffuse out to the surface and due to the high surface tension of the water (liquid) make it impossible to adapt liquid solvent anymore.

Also, existing chemicals added to the UPW to clean is extremely toxic to human beings as well as the environment. We must resolve these environmental problems in wafer industry in the immediate years to come. Besides, in a single fab line, there are more than thirty cleaning stations. The cleaning units in the front end fab line, the photoresist material is not yet etched and it is already developed supercritical leaning method. The problem lies in the back end fab line where the resist polymers are degraded due to the plasma etch and worldwide attention in researching the supercritical solvent cleaning is focusing into the cleaning unit in the back end fab line. Present work, interest is placed on the cleaning of the etched photoresist materials.

Experimental Results and Discussion

Three different experimental apparatuses were originally designed and constructed in the present work. However, the basic principle and units in a complete cycle of the supercritical cleaning process is nothing new with existing information and we omit here the details of the schematic feature of the processes.

To practically implement the present experimental efforts to replace a few of existing wet stations among many of them in existing wafer fab line, experimental target of the cleaning experiments are limited to both the cleaning of plasma etch hard baked photoresist residue after photolithography and cleaning unit of the resist residue after the aluminum metal etch step. These two candidate cleaning units can be regarded as the most challenging problems in conjunction to the replacement of the supercritical cleaning to the existing wet cleaning. Also, from a semiconductor company, the real high aspect ration patterned wafers as well as bare wafers before and after plasma etching samples are used directly in the experiments.

In the present work, a long-time effort is placed on searching the property modifiers and several pure substances are newly found and tested individually the removal performances, respectively. Upon scrutiny of these experimental runs, we concluded that most of the pure modifiers do not satisfy the designated cleaning performance. Thus, based on these preliminary experience, we tried to formulate several different types of mixed modifiers with different recipes and tested again the cleaning performance of each mixed modifiers. Fortunately we could found that the modifiers temporarily named as GT011 and GT012 was surprisingly successful to remove completely the resist residue in both the sample patterned wafers. These results were comparable with the cleaned sample by the existing wet cleaning with UPW.

For the two mixed modifiers, the effect of amount of addition and the operation conditions are conformed and again we can concluded that these two mixed modifiers will accelerate the practical implementation of the supercritical carbon dioxide-based dry cleaning in wafer industry. On-going work is placing similar type of searching new recipes of mixed solvent and subsequent experimental conformation and in this regard, this work can be regarded not a complete discussion but an interim report and it is a reason this article stay as qualitative description rather than more quantitative one.

Concluding Remarks

In recent years encouraged by increased stringent environmental regulations on the release of toxic chemicals and costs of UPW and solvent use in wet cleaning stations, the semiconductor industry is eager to abate chemical and UPW usage in wafer fabrication lines. Thus, it is imperative to find any technological alternative to replace such wet cleaning station by environmentally responsible cleaning method. Among many new ideas, the dry cleaning without using UPW and with greener solvents such as carbon dioxide is gaining interests.

During this decade, many worldwide investigators have been focus their attention on the replacement of wet cleaning by the new supercritical carbon dioxide cleaning. However, due to its intrinsic limitation of solvent property, no one yet obtained practical research results for commercial prominence.

During the last four years, the present authors also placed their interests on resolving the drawbacks of the underlying supercritical carbon dioxide with expectation of practical commercialization in mind. As results, they found a new recipe of mixed modifiers. By these candidate modifiers added to the supercritical carbon dioxide, cleaning experiments were performed successfully for the real patterned wafers after the plasma etched and aluminum metal etch. These results seemed to be very promising and the authors wish these results will be an addition in new nonaqueous cleaning in semiconductor industry.

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