Solvent and Semi-aqueous Chemistry Applications

Introduction

Within the semiconductor manufacturing flow solvent-based processes are used for cleaning the wafer surface and remove photoresist at steps in which inorganic chemistries cannot be used. In particular when metals are present on the wafer conventional sulphuric peroxide (SPM) or SC-1 solutions are not applicable, since the peroxide will react with the metal. Typical applications for solvent or solvent containing wet processes are resist stripping and polymer removal in the back end of line (BEOL) and wafer level packaging. Various materials and contaminants need to be removed without attacking the Cu and Al lines or the low-k dielectric. Figure 1 shows an overview on the most prominent tasks of solvent or SAC processing in the BEOL, using Cu and Damascene process schemes.

Figure 1. Schematic illustration of the variety of contamination present in a dual damascene process (1).

Recently solvents or solvent containing solutions are discussed during the formation of the transistor in the front end of line (FEOL) for high dose implanted layers, where the crusted photo resist cannot be taken away in conventional SPM wet strips without applying additional dry processes in a plasma. With the process margins for strip and clean with respect to Si and SiO_2 loss dramatically being reduced for 60 nm or below devices dry plasma stripping is increasingly difficult since the surface is roughened and attacked. An all wet solution providing sufficiently low defect density and capability of taking off the resist completely without substrate or structural damage might become an alternative for advanced devices

Applications of solvent or semi-aqueous chemistry in wet chemical processing can be divided into three major tasks:

1. Resist removal: Semiconductor devices are formed by a sequence of layer depositions, which are patterned by lithography and subsequent anisotropic (dry) etching or ion implants. The resist protecting those areas on the wafer not to be modified must be completely removed without attacking the surface before a new layer and deposited. Preferably this is done in a combination of dry plasma ash, an inorganic strip by oxidation of the resist polymers and subsequent wet cleaning, but solvents are used where neither dry methods nor strong oxidizers can be applied because of damage of the open surface. Solvents remove the resist by full dissolution.

2. Polymer removal: Anisotropic etching in a plasma processor is achieved by electrostatic potentials accelerating the reactive species towards the wafer surface, but also by in situ passivation of the sidewalls by reaction by-products in order to prevent lateral etching. These polymers have a more or less undefined consistence including organic and inorganic components. Inorganic plasma or wet stripping often does not remove theses polymers. Solvents with an oxide removing component (typically HF) combine etching and dissolving characteristics and are effective to take away the polymers,
3. Lift Off processes: Lift Off is a special method of taking away organic layers, in particular when covered with an inorganic or metal top layer. In particular at wafer level packaging large metal lines are formed by putting on and patterning the resist first and then deposit metal on the entire surface. Lift off is used to remove the deposited metal from unwanted areas by detaching the organic resist underneath and remove the metal together with the resist.

Characteristics of Solvents and Semi-aqueous Solvents

Solvents are defined as a material that can dissolve other materials without chemically interacting with them. Although solvents can be of different aggregation states, most solvent and in particular those relevant for wet chemical processing of semiconductors, are liquids. Solvents are typically organic molecules and can be divided into those with non-polar and polar behavior. Non-polar solvents have the hydrogen atoms fixed to the carbon chains and therefore are nonconductive. They can dissolve and are miscible very well among other solvents and with other organics chemicals. Polar solvents have functional groups built into their molecular structure that allow dissociation of protons and therefore can also interact with other polar molecules.

The use of solvents for resist stripping and polymer removal has evolved continuously over the last years. For semiconductor applications hundreds of different solvent and semi-aqueous mixtures have been and there are many in development to meet enhanced process requirements, such as smaller device ground rules, increasing wafer size new materials (*i.e.* Cu, low-k, and metal gates) and environmental protection. Therefore only a general overview will be given:

Purely solvent-based mixtures for resist stripping: These chemicals swell the organic polymers of the resist and dissolve it at temperatures below their respective boiling point. Examples are NMP, n-BA/IPA or PGMEA. Figure 2 shows an overview of thermo-chemical characteristics. Since most of these solvents are not water soluble, an additional process step with IPA is required for rinsing (see next section).

Figure 2: Overview of thermo chemical properties of pure solvent for semiconductor applications (3).

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Amine based strippers: As dry etching processes evolved it became necessary to remove etch residue and photoresist during the post-etch cleaning process. Polar organic solvents provide better results for removing typical etch residue and at the same time are able to remove the organic resist chains. Amine-based products were introduced containing one or several amines (typical hydroxylamine and ethanolamine) a corrosion inhibitor and water. Examples of these types of solvents are ACT 935, ST-22, or EKC-265. Due to the water content these solvents do not require additional solvent rinsing. Typical process temperatures are in the range of 50 to 75°C.

Fluorine containing strippers: Initially hydrofluoric acid was used with glycol in the FEOL to simultaneously etch silicon oxide and silicon nitride, but more dilute aqueous solutions are used in BEOL polymer removal which include an HF salt (typically NH4F).

Although these mixtures work well on inorganic material removal they are not capable of stripping photoresist and have limited capability with respect to removal of material when Al or Cu are present. Typical examples are ATMI NOE, ST-200, or ACT NE-12,

pH buffered strippers: Solutions, both solvent or aqueous based with a controlled pH value are required to control the etching of the low-k dielectrics of advanced semiconductors. These solvents are easier to use on single wafer equipment, since their viscosity is low and processing is done at ambient or moderately elevated temperatures (< 50°C). Examples of these media are EKC-6xx, ATMI ST-250, Baker ALEG or REZI, and ACT BNE products. All of these mixtures are proprietary to the chemical manufacturers.

Overview on Solvent and Semi-aqueous Solvent Equipment Processors

Batch processors have been the primary choice for solvent processing. Resist stripping in wet immersion benches has been in use for years, in particular for applications in the BEOL and wafer level packaging, when inorganic stripping is not applicable due to the presence of metals. Due to the configurability of the equipment solvent benches can be used for polymer removal, both in the FEOL and after metallization. Solvent and semi-aqueous batch equipment should have recirculation and replenishment systems. Rinsing and drying is done on the same platform, as long as cross contamination is avoided. Process times varied between 20 – 60 minutes (depending on the type and thickness of resist). Chemical usage can be optimized by multiple use of the medium with partial replenishment. Disadvantages are high defect rates (particles), filtering of the recirc ulating solution help with this issue. Intermediate rinses (if needed) can be implemented without loss in productivity. The performance of the strip or clean is enhanced by ultrasonic or physical agitation. Although in principle feasible for new advanced chemical mixtures immersion processing does not play a major role in low k/Cu applications, due to lack of wafer-to-wafer process control and the amount of chemicals needed in immersion baths in single pass mode. However with the return to all wet processing and the cost of proprietary chemicals advanced re-circulating systems might become a cost effective alternative for some of the processes currently done on single wafer equipment.

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Process sequences and parameters of solvent and SAC processing in wet benches

A specific process flow for solvent resist stripping as well as strip and polymer removal with semi aqueous chemistry depends on a number of factors outside the wet process itself like:

- Type, thickness and pretreatment of the resist
- Type of solvent used in the process
- Specific step and application in the process flow.

Therefore only base processes for solvent strip (non water soluble) and semi aqueous chemistry clean or strip are given with a typical range of parameters and performance criteria.

Process time: 10 – 20 min
Temperature: 65- 75 °C

Recirculation flow: 6 -8 gpm
Filtration: 0.1 – 0.2 µm
Optional:: ultrasonic or wafer movement
Bath life: chemical dependent 12- 36 hrs.

Same as solvent strip 1

uses fresh chemistry
Optional: Ultrasonic or wafer movement

Medium: IPA ambient
Process time: 5 -10 min
Recirculation flow 6 – 8 gpm
Filtration: 0.1. µm

Process time : 5 min
Temperature ambient

Rinse flow 8 -10 gpm

Spin / rinse or surface tension dry

Process time app. 10 min

ss sequence applies for example for resist removal with NMP or PGMEA. The intermediate rinse step is required only if the solvent water and thus the process chemical will not be taken way efficiently in an ultra pure water overflow rinse. However most solvents olvents and can be displaced from the surface with water soluble solutions like Isopropanol alcohol . Rinsing for such solvents in a two step process, in which first the insoluble solvent is replaced with a water soluble and second the water soluble solvent is The two step rinse replaces a very long, but still inefficient UPW rinse of 30 – 45 min and thus is justified both from cost and iew. In particular when surface tension gradient drying is used, the drying performance will be impacted if substantial residues of e wafer prior to the drying step.

criteria:

remaining photo resist after process

attack or damage (corrosion) of structures

ticle: < 30 particles added per process

watermarks

ess performance is determined primarily by the choice of the chemical and its properties. Critical factors beside the chemical ong time process stability and direct chemical wafer interaction. In wet benches this is achieved by optimal flow control and wafer oving the substrates in the solution or introducing ultrasonic or megasonic energy. However in particular for small feature sizes t damage structures and thereforeultrasonic (at frequencies below 250 kHz) or even mega-sonic (> 250 kHz) do more harm then must be setup individually for each product and application by the end user.

/ for semi aqueous polymer removal (f.e. using ATMI's ST250 or Dupont's EKC 6xx chemistry) in a wet bench consists of the

Process time: 5 – 20 min

Temperature: 45-60 °C

Recirc flow: 6 -8 gpm

Filtration: 0.1 – 0.2 µm

Optional:: ultrasonic or wafer movement
Bath life: chemical dependent 12- 36 hrs.
Re-plenishment chemistry dependent

Same as solvent strip 1

Process time : 5 min
Temperature ambient
Rinse flow 8 -10 gpm

Spin / rinse or surface tension dry
Process time app. 10 min

ss sequence applies for example for polymer removal in the BEoL. Depending on the chemistry it s applicable for Al or Cu
water base of the mixture a normal rinse is sufficient to take of the organic components.

criteria:
remaining photoresist or polymers after process
attack or damage of structures(Cu corrosion)
attack of low k material or change of k -value
ticle: < 30 particles added per process
watermarks

iderations for immersion equipment

›nly used solvents are combustibles (flammable materials) and have a significantly lower flash and boiling point than other media
ng of semiconductors. With no conductive material present (f. e. metal containers, process chamber, piping) they can built up
by flowing inside non-conductive tubes. The result (except for substrate damage) might be self ignition causing explosive reactions
ining atmosphere. The flash point is the temperature at which the liquid's vapor pressure is high enough to provide an explosive or
'e. Flash and boiling point are chemical specific, as well as the atmospheric concentration range, in which a combustible vapor can
›ment design as well as the process conditions must ensure that no time an flammable or explosive atmosphere can form. National
ıdards like S2 or NFPA 79 require compliance not only during normal operation but also under single fault conditions (fault
›ccur be a single root cause). Process fumes are exhausted to an non-flammable exhaust line (typically made of stainless steel) and
be designed that at no time inside and around the equipment fire or health hazard are formed. Design and verification requirements
ɪrnational ATEX standard. This standard includes regulations about the choice of piping material and components. In general all
ıt must be solvent compliant and certified for the use under the conditions determined for the process.

ıost solvent are toxic or present other hazard to humans. Therefore special care must be applied when solvent are used in
ssing. In order to assess the risk of hazards in particular in the U.S. all solvents and solvent processing equipment are labeled with
ıond shown in Fig. 2.

;

'rds reactivce (chemical) hazards

ds (to be nominated)

amond [2]

iamond is broken up into four smaller diamonds representing different types of hazards. The BLUE section denotes health hazards,
›tes fire hazards, and the YELLOW section denotes reactive hazards. The forth diamond, WHITE, is left blank unless there is a
as oxidizers, water reactives, or radiation hazards.

e three colored diamonds, there will be a number ranging from zero (0) to four (4). Zero represents relatively no hazard and four erous material. For details on hazard risk assessment refer to the websites of national or international standard committees like al fire protection association) etc. (www.semi.com/standards/ or (www.nfpa.com or for more standard information lu/researchservices/ehs/generalsafety/facilities/nfpa.html).

tion for the chemicals including the specific safety diamond rating is available in the materials safety data sheets (MSDS), available on the web.

re risk most IC manufacturers require fire extinguishing means integrated in the equipment. Depending on the chemistry used this ater sprinklers or CO2 extinguishers above the process tanks and the chemical treatment section (recirculation, prepping areas).

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