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The effects of supercritical CO_2 formulations on the removal of high-dose ion-implanted photoresists

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ABSTRACT

A new effective method for high-dose ion-implanted photoresist (HDI PR) stripping is reported based on supercritical CO_2 ($scCO_2$) microemulsions consisting of branched hydrocarbon surfactant 2-ethylhexanol polyoxyethylene–polyoxypropylene (EH-3) and co-solvent dimethylsulfoxide (DMSO). The optimized concentrations of EH-3 and DMSO in $scCO_2$ were 3 wt.% and 2 vol.%, respectively, and the weight ratio of H_2O and EH-3 is 1:1. The HDI PRs containing crust layers were removed in the $scCO_2$ microemulsions at 10–25 MPa and 40–80 °C for 20 min. The results revealed that the stripping efficiency of HDI PR increased with the pressure and temperature (T) when T is lower than 60 °C. The removal efficiency of 96.8% was achieved at 60 °C and 20 MPa and then it gradually decreased as T higher than 60 °C due to the lower $scCO_2$ density at higher T. Magnetic agitation was favorable for the HDI PR removal. The optimum stripping parameters were determined to be 60 °C and 25 MPa for 20 min at which 100% removal efficiency was achieved in EH-3/DMSO/$scCO_2$ microemulsions. This environmentally benign method provides a promising alternative to effectively strip HDI PR for devices with nano-sized feature dimensions in microelectronic processing.

1. Introduction

The effective removal of high-dose ion-implanted photoresist (HDI PR) in IC manufacturing process has become more challenging as the number of photoresist steps has increased while the allowable material loss and surface damage has decreased with the chip size downscaling. Heavily implanted photoresist is difficult to remove because this crust is insoluble in wet chemicals, since an amorphous carbonized crust is formed due to the reaction of the implanted cation with the photoresist polymer when the ion-implant dose is greater than 5×10^{14} atoms/cm^2 [1]. The removal of HDI PR has been conventionally achieved through a combination of dry plasma ashing and a subsequent wet chemical treatment at elevated temperature [2–4]. These physical and chemical approaches can not only lead to the increase in material loss and damage to fine structures but also are troublesome due to chemical disposal cost, ultrapure water consumption, and other environmental burdens [5]. Furthermore, with the feature size continuing to shrink, HDI PR residue in the trench/vias of high aspect ratio structure is difficult to remove in aqueous-based cleaning solutions due to high surface tension and capillarity. The remaining residues at the bottom of the trench/vias will increase the contact resistance of interconnects, which will affect the subsequent process and eventually degrade the device performance. To fabricate smaller devices, low conductivity (ρ) copper and low dielectric constant (k) insulators are usually required to replace Al and SiO_2 as interconnects and inter-metal dielectrics, respectively, to minimize the resistance–capacitance (RC) coupling which gives rise to interconnect delays, cross-talk noise, and power dissipation. However, the aqueous-based cleaning solutions will cause the corrosion of Cu lines and an increase in k values due to the diffusion of water into the low-k porous dielectrics used in back-end-of-line cleaning processes [6]. Oxygen-based photoresist ashing can also change the properties of low-k insulators [7]. To alleviate such problems, superior alternative HDI PR stripping and residue cleaning methods with environmental considerations need to be developed.

Recently, supercritical CO_2 ($scCO_2$) has been proposed as a promising cleaning medium for photoresist stripping [8–10]. The properties of near zero surface tension and tunable solvating ability in conjunction with its advantages of moderate critical temperature and pressure, nonflammability, ease of availability, low cost, and being environmentally benign render $scCO_2$ an attractive solvent in a variety of applications in microelectronic manufacturing [11–13]. $scCO_2$ can easily penetrate into small holes, polymer films, and the interfaces between photoresist and the underlying substrate due to its low surface tension. Therefore, the penetration of $scCO_2$ into the hard carbonized crust and the interface expands the crust and weakens the adhesive force thereby facilitating

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lifted-off from the substrates [14–16]. However, scCO$_2$ is not a good solvent for polar species or polymers like photoresists because of the small cohesive energy and zero dipole moment. Previous studies have shown that the addition of co-solvents and/or surfactants into scCO$_2$ can enhance solvent strength of scCO$_2$ [8,17,18]. Hess [18] investigated the effect of scCO$_2$/tetramethylammonium hydroxide (TMAH) mixtures containing methanol and water on the removal efficiency of post-plasma-etch residues. The results showed that a 12 wt.% of a 4:1 volumetric mixture of 25% TMAH in methanol and deionized water in CO$_2$ at 3000 psi and 70 °C was effective in removing the residues. Chao [19] found that the pause flow method using scCO$_2$ containing ethyl acetate co-solvent could strip polymethylstyrene derivatives type photoresist (YSB 663) better and 94.6% removal efficiency of 600 nm PR spin-coated on 500 nm Cu were obtained at the optimum conditions of 120 °C, oven temperature; 350 atm, CO$_2$ pressure; 0.2 ml of ethylacetate spiking to scCO$_2$; 2.0 min, static equilibrium time; and five cycles of dynamic flow pausing. Their results also showed that photoresist coated on Cu alloy were more difficult to remove than that on Al.

Fluorine and silicon-based surfactants were first used to form scCO$_2$ stable microemulsions due to the high solubility in scCO$_2$ [20,21]. While hydrocarbon-based surfactants are difficult to dissolve in scCO$_2$, co-solvents and specific additives are usually added to increase the solubility of hydrocarbon surfactants in scCO$_2$ [22–24]. Branched alkyl hydrocarbon surfactants formed by methylation of chain tips have higher solubility in scCO$_2$ than linear chain hydrocarbon surfactants due to their good affinities with scCO$_2$ and large steric volume of CO$_2$-philic groups [25,26]. The post-etch residues in vias and trenches in patterned low-*k* porous methylsilsesquioxane (pMSQ) interlayer dielectrics were removed in solutions containing branched hydrocarbon surfactant polyoxyethylene 2,6,8-triethyl-4-nonyl ether (5b-C$_{12}$E$_8$), water, and scCO$_2$ [27]. The low interfacial tension induced by surfactant and scCO$_2$ is beneficial to the decrease in the Laplace pressure to facilitate both penetration and HDI PRs removal. In this work, we report the stripping behavior of HDI PRs in scCO$_2$ microemulsions containing highly branched hydrocarbon-based surfactants 2-ethylhexanol polyoxyethylene–polyoxypropylene (ECOSURF™ EH) or 2,6,8-trimethyl-4-nonyl poly(ethylene glycol) ether (TERGITOL™ TMN) with dimethylsulfoxide (DMSO) or 2-propanol (IPA) as co-solvents. The surface morphology and photoresist stripping efficiency were evaluated by combining optical microscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS). The effects of the type and concentration of surfactants and co-solvents, the ratio of water to surfactant, temperature, and pressure on the removal rate were investigated. The optimum cleaning parameters were achieved and a mechanism for photoresist stripping in scCO$_2$ microemulsions is suggested.

2. Experimental

ECOSURF™ EH-3 and TERGITOL™ TMN-3 were purchased from Dow Chemicals (Shanghai) and used as hydrocarbon-based surfactants in scCO$_2$ microemulsions. The chemical structures of EH and TMN are shown in Fig. 1. The average number (n_{avg}) of hydrophilic ethylene oxide (EO) groups for both surfactants are around 3 and the calculated average molecular weights are about 523 and 318 for the EH and TMN (named EH-3 and TMN-3), respectively. Analytical grade of DMSO and IPA were purchased from Aldrich and used as co-solvents. The samples were the same as those used in a previous study [28]. Herein, TaN film was chosen because photoresists coated on metal alloy were more difficult to remove than those on SiO$_2$ [29]. The wafers was cut into 1 × 1 cm^2 pieces and used as the treated samples.

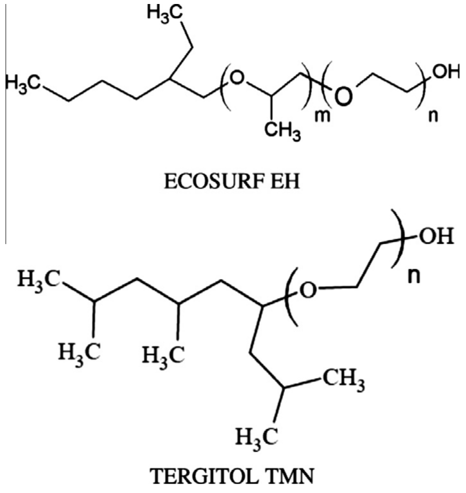

Fig. 1. Chemical structures of surfactants ECOSURF EH and TERGITOL TMN. $n_{avg} = 3$ for EH-3 ($M_w = 523$) and TMN-3 ($M_w = 318$).

The high pressure cleaning system used for stripping HDI PRs in scCO$_2$ microemulsion consists of a 200 ml hastelloy alloy chamber equipped with a magnetic agitator, an ISCO high pressure syringe pump (model 500D), and an equilibration cell for surfactants and co-solvents. The details of this system can be found in a previous study [28]. A magnetic agitator was used to maintain homogeneity of the scCO$_2$ microemulsions, to elevate the dissolution of the stripped photoresist, and to enhance the reproducibility. The weight percent of surfactant was calculated by dividing the weight of surfactant by the total amount of surfactant and scCO$_2$ in the chamber. The weight of scCO$_2$ was determined by the chamber volume and scCO$_2$ density at the given temperature and pressure [30]. The wafer sample was first loaded into the cleaning chamber which was already heated to the desired temperature (40–80 °C), and the calculated amount of surfactant and/or co-solvent were injected into the equilibration cell using a micro-syringe. Before fully delivering the required amount of scCO$_2$ into the high pressure chamber, a small amount of scCO$_2$ at the lower pressure than required was first flowed into the equilibration cell to guarantee homogeneity for the mixture of surfactant and/or co-solvent in CO$_2$. The depressurized pure CO$_2$ (99.999%, Deyang Co., China) was delivered into the cleaning chamber through the equilibration cell by means of an ISCO syringe pump previously filled with fully liquefied CO$_2$ through the low-temperature water bath (2 °C). Cleaning time was tabulated when the temperature and pressure reached the designed values. The designed temperature and pressure can be achieved within 1 min with a pre-heater in the pipeline. After the cleaning process ended, the scCO$_2$ microemulsions were vented into a separating trap to collect any residual chemicals (including photoresist residues) during the phase separation and then followed by several rinses using fresh scCO$_2$ with pressure higher than the desired one. For every designed experiment, at least three trials were conducted to obtain the average removal rate. The standard deviation was controlled to be within ±0.5%.

The surface morphology and photoresist residue were characterized using optical microscopy, FT-IR, XPS, and SEM techniques. In general, the photoresist removal rate was calculated by dividing the stripped area by the original photoresist area in pixels which was determined using a metallurgical microscope. FT-IR and XPS measurements were also used to confirm the calculated removal rate by dividing the sum of area of the radical peaks for the cleaned sample by that for the as-obtained one. The area of the radical