Novel photoresist stripping technology using steam-water mixture*

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Abstract: A novel wet vapor photoresist stripping technology is developed as an alternative to dry plasma ashing and wet stripping. Experiments using this technology to strip hard baked SU-8 photoresist, aurum and chromium film are carried out. Then the images of stripping results are shown and the mechanism is analyzed and discussed. The most striking result of this experiment is that the spraying mixture of steam and water droplets can strip photoresist and even metal film with ease.

Key words: photoresist stripping; plasma ash; wet stripping; steam-water mixture; jet spray

DOI: 10.1088/1674-4926/32/2/026001 **EEACC:** 0170G; 2550G

1. Introduction

Because negative photoresist cross-links when exposed to UV light, these thick negative photoresist layers are extremely difficult to strip with traditional strippers that work by swelling and dissolution. In this research, negative photoresist SU-8 is chosen. SU-8 is designed for micromachining and other microelectronic applications, where a thick chemically and thermally stable image is desired. The exposed and subsequently cross-linked portions of the film are rendered insoluble to liquid developers. Microchem's remover PG swells and lifts off minimally cross-linked SU-8. It cannot remove fully cured or hard baked SU-8. Several methods of photoresist stripping have been reported, including the traditional wet process[1, 2], ozone/DI water[3–6], oxygen plasma[7] and UV/ozone[8]. But these methods have either limitations or high consumption of chemicals. Additionally, supercritical carbon dioxide has been considered as a potential technology in photoresist stripping process[9–14]. At present, however, the total stripping time of this method is too long to be generally accepted. In this paper, an alternative removal process is proposed. This produces high-speed steam and purified water droplet mixture that is sprayed on the surface of a silicon wafer coated with SU-8 photoresist. The most important feature of the process is that we use water only; hence, we are able to strip the photoresist without chemicals. This novel technology significantly reduces any effect on the environment, health and safety, while enabling achievement of the international technology roadmap for semiconductors' (ITRS) goals.

Up to now, only a few researchers, such as Sanada *et al.*[15, 16], have practised the general mechanism to explain this process. In the following, doing some experiments on hard baked SU-8 photoresist, aurum and chromium film, we reach a conclusion that both momentum transfer and enhancement of solubility of polymer play an important role in the cleaning process.

2. Experiments

2.1. Reagents and chemicals

Analytical grade sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), ammonium hydroxide (NH_4OH), dilute hydrofluoric acid (HF), hydrochloric acid (HCl), acetone (C_3H_6O), methanol (CH_3OH) and deionized water (DIW) were used as rinsing solvents without further purification.

2.2. Wafer sample preparations

First, silicon wafers were cleaned by standard RCA cleaning processes to remove organic contamination, particles and native silicon dioxide on the surface, and rinsed thoroughly with DIW. They were then carefully cleaned in an ultrasonic bath with acetone, methanol and DIW subsequently for 10 min each. Finally, wafers were blown dry with ultrapure compressed N_2 gas, and baked in a vacuum-suction oven at 180 ℃ for 2 h to completely remove any moisture.

2.3. Resist processing

The steps of resist processing are listed in Table 1. Negative photoresist SU-8 (MicroChem Corp.) was dispensed on the cleaned wafer samples and spin-coated with 3000 rpm for 1 min. The film thickness was 10 μm, according to Ref. [17] (MicroChem Corp.). Post-apply bake (PAB) treatment was performed with a two-step contact hotplate process: 65 ℃ for 120 s and then 95 ℃ for 120 s to evaporate the solvent and densify the film. The pattern was generated by lithography apparatus EVG 620 (EV group, KK, YOKOHAMA, JAPAN), then baked also with a two-step process: 65 ℃ for 60 s and 95 ℃ for 120 s to cross-link the exposed portions of the film, then finally hard baked in an oven (DZF-6050,YaShiLin Corp. Beijing, China) at 200 ℃ for 2 h. These wafers were cleaved into small pieces, each having hard baked SU-8 photoresist.

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* Project supported by the National Natural Science Foundation of China (No. 60976017).

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Received 29 June 2010, revised manuscript received 27 September 2010

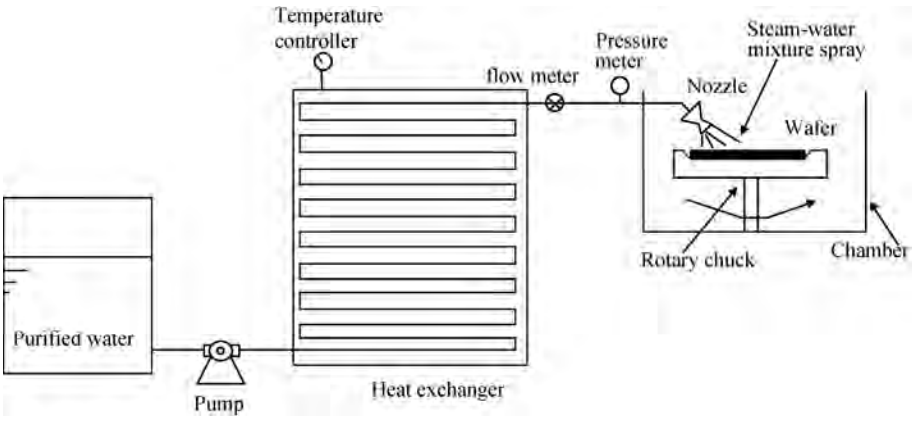
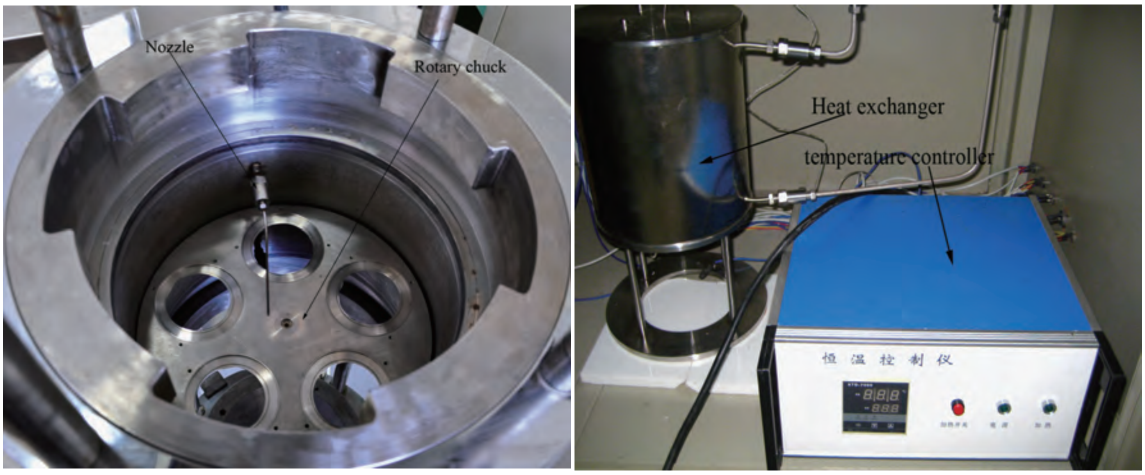


Fig. 1. Schematic of steam-water mixture spray system.



(a) (b)

Fig. 2. Experimental apparatus. (a) Chamber with rotary chuck and nozzle. (b) Digital temperature controller and heat exchanger.

Table 1. Steps of SU-8 photoresist processing.

Step	Condition
Spin	3000 rpm, 1 min
PAB	65 ℃, 120 s; 95 ℃, 120 s
Exposure	185 mJ/cm^2
PEB	65 ℃, 60 s; 95 ℃, 120 s
Development	120 s
Hard bake	200 ℃, 2 h

2.4. Instruments

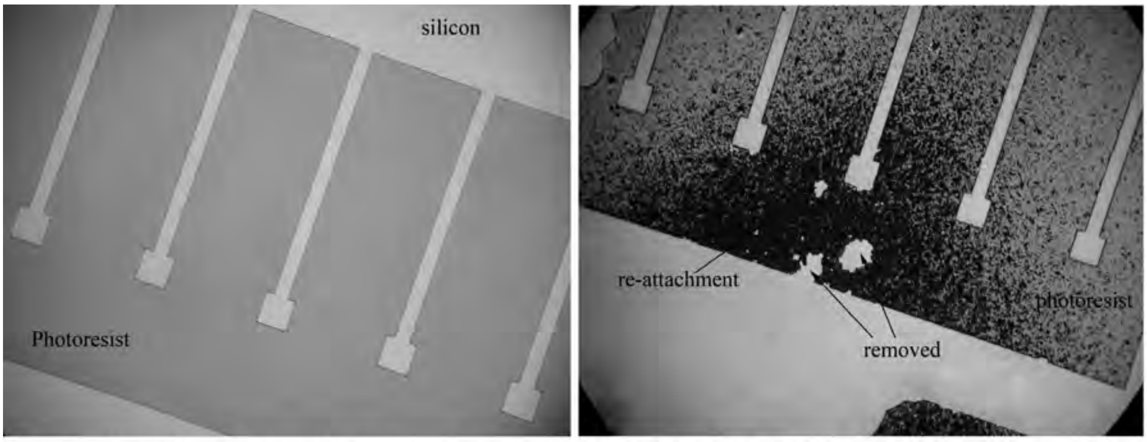
A schematic of equipment used for photoresist stripping with a combination of steam and water droplets is provided in Fig. 1. This consists of a high pressure syringe pump, a temperature-controlled heat exchanger where water absorbs heat and is evaporated into steam, a stainless steel chamber, a digital temperature controller used to keep the temperature of the heat exchanger constant, a rotary chuck, a nozzle through which mixture is sprayed onto the surface of the wafer, a flow meter and a pressure meter utilized to measure the flux and pressure of the fluid, respectively. The actual experimental apparatus is shown in Fig. 2.

2.5. Experimental procedures

First, we put the wafer sample on the rotary chuck and heated the heat exchanger. When the heat exchanger reached the desired temperature, we adjusted the flow meter and opened the related valves to let water flow into the heat exchanger to absorb heat. During this process, water partially evaporates into steam, then steam and water droplets are mixed in the tube. This mixture is accelerated in a special nozzle and sprayed on the surface of wafer sample. In this process, the chuck may have rotated to enhance the stripping efficiency. The water flow rate and the heat exchanger temperature range from 200 to 500 mL/min and 200 to 500 ℃, respectively. The distance and the angle between the nozzle and the surface of wafer were set at 5 mm and 45°, respectively. The stripping results were observed by optical microscope (BH3-SIC6, Olympus Optical Co. LTD, JAPAN).

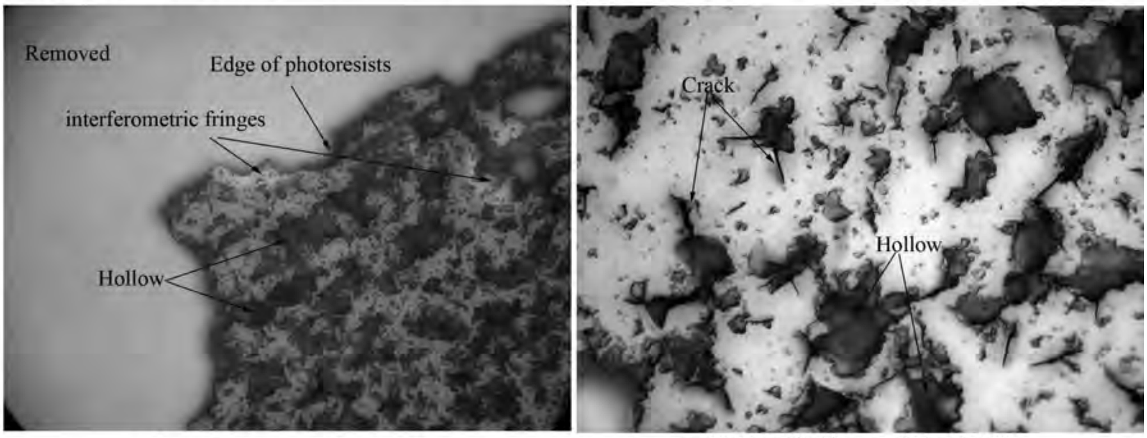
3. Results and discussion

Using this spray of steam and water droplet mixture, the hard baked SU-8 photoresist was successfully stripped. Images of photoresist stripping are shown in Fig. 3. This result clearly indicates that the photoresist is lifted off and breaks up into



(a) Hard baked SU-8 photoresist before cleaning. ×100 (b) $T = 270$ ℃, $P = 2$ MPa, $Q = 0.35$ l/min, $t = 15$ s. ×100

(c) $T = 300$ ℃, $P = 2$ MPa, $Q = 0.35$ l/min, $t = 30$ s. ×500 (d) $T = 350$ ℃, $P = 3$ MPa, $Q = 0.35$ l/min, $t = 30$ s. ×100



(e) Magnified image of (d). ×1000 (f) Magnified image of (d). ×1500

Fig. 3. Microscope images of SU-8 photoresist stripping.

pieces with certain sizes. And a re-attachment of stripped fragments of photoresist is obviously observed in Figs. 3(b) and 3(c).

Photoresist cleaning in hydrothermal environments can be affected by three types of water property: (1) thermodynamic properties (P–V–T relationships of water and phase behavior of steam-water mixture); (2) solution properties (dielectric constant, electrolytic conductance, dissociation constant, and hydrogen bonding); and (3) transport properties (viscosity, heat capacity, diffusion coefficient, and density). All of these properties change when the temperature and pressure of the water change.

As shown in Figs. 3(e) and 3(f), there are some cracks or holes in the region where the mixture is sprayed. According to this result, the reason why the proposed technology is able to strip the photoresist may be the effect of moisture penetration. Sanada *et al.* have reached a conclusion that, during this stripping process, the steam-water mixture decreases the adhesion between the photoresist and silicon surface with moisture penetration into the boundary[15]. In order to justify their conclusion, they add deuterium oxide into the steam-water mixture, which is then sprayed onto a wafer, and use mass spectrome-

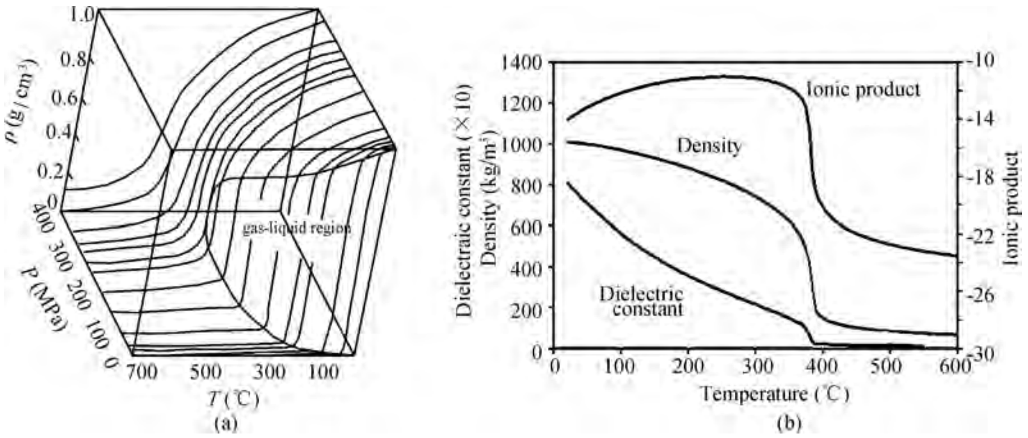
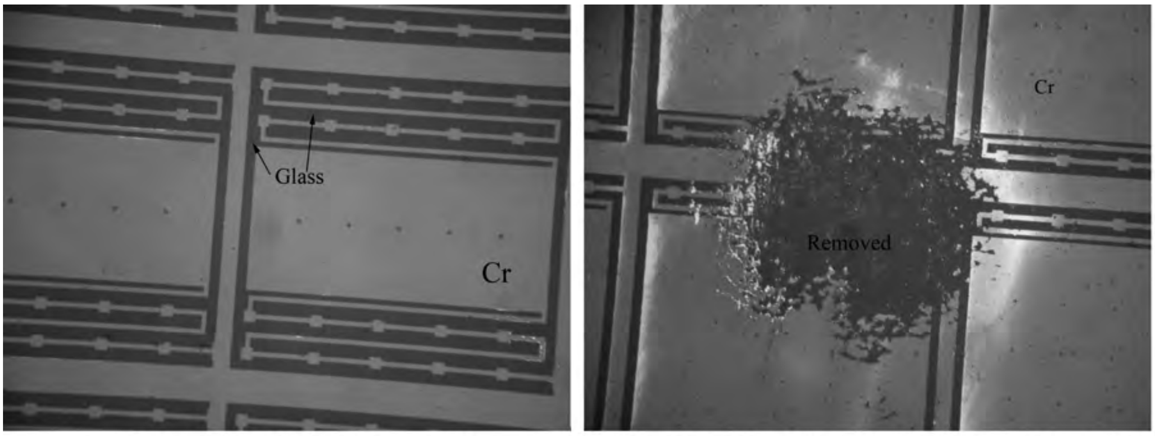
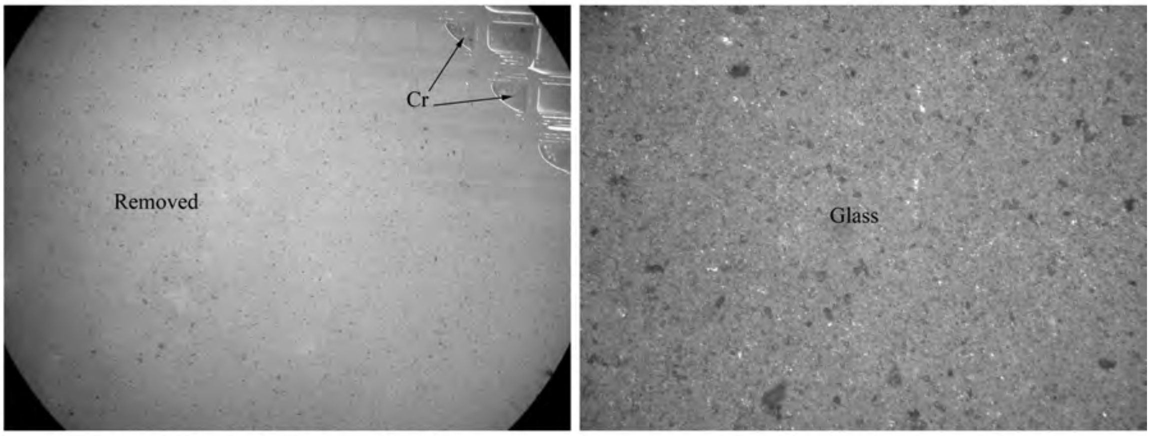


Fig. 4. Physical properties of water versus temperature and pressure. (a) Density of water versus temperature and pressure. (b) Physical properties of water at a pressure of 24 MPa versus temperature.



(a) Chromium film before cleaning. ×500 (b) $T = 330$ ℃, $P = 2$ MPa, $Q = 0.35$ l/min. $t = 60$ s, ×500



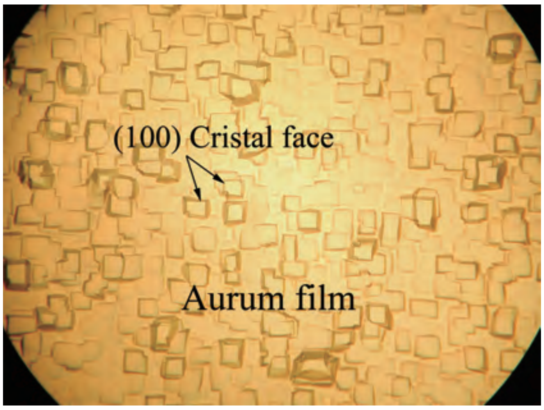
(c) $T = 330$ ℃, $P = 2$ MPa, $Q = 0.35$ l/min, $t = 60$ s (at the same point). ×100 (d) Magnified image of (c). ×1000

Fig. 5. Microscope images of chromium film stripping.

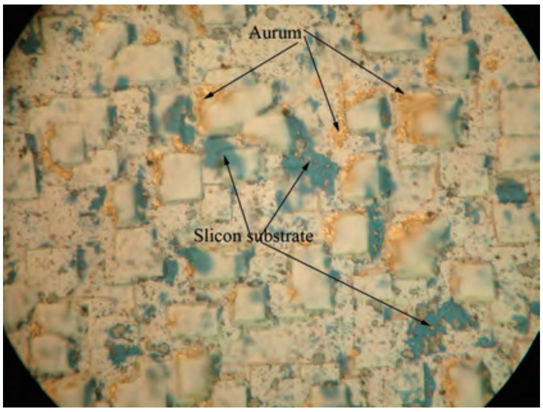
try to measure the amount of moisture penetration. The results show that deuterium oxide does penetrate the photoresist.

It is also believed that there exists an effect of momentum transfer during the spray processing. So we used the mixture to strip chromium film on photomask to observe the effect. The thickness of chromium film was 0.1 μm. Images of chromium film stripping are shown in Fig. 5. The result clarifies that the steam-water mixture can also strip chromium film where the mixture is sprayed.

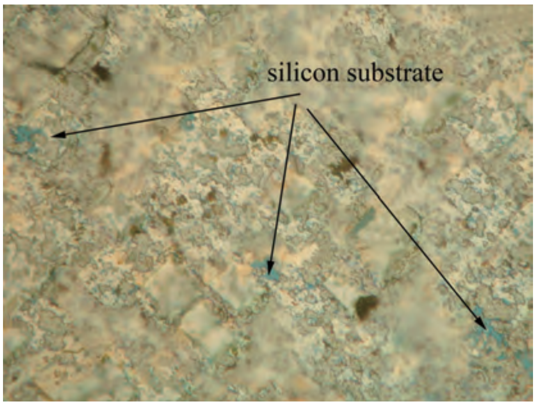
The reason why the chromium film is stripped by a steam-water mixture is because chromium happened to be oxidized during the process, because the chromium is not stable in most conditions. In order to verify the theory, we use aurum film to repeat the experiments. The thickness of the aurum film is 0.2 μm. Fortunately, aurum is easily stripped by this technology, which indicates that there may not have been an effect of oxidation during the process since the aurum is a kind of stable element in nature. The stripping results are shown in Fig. 6. The



(a) Aurum flim before cleaning. ×1000



(b) T = 380 ℃, P = 2 MPa, Q = 0.35 l/min, t = 90 s. ×1000

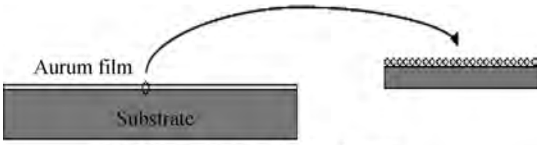


(c) Magnified image of (b). ×1500

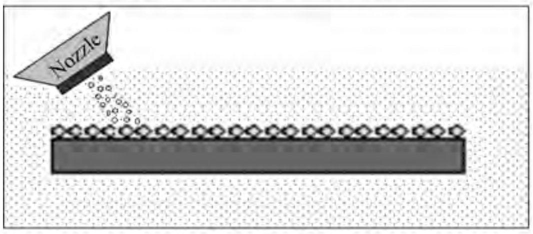
Fig. 6. Microscope images of aurum film stripping.

most likely reason is that the high speed fluids generate high impact at the surface. The theory is similar to that of metal abrasives, which has been proved by Sanada *et al.*[16], on different metals.

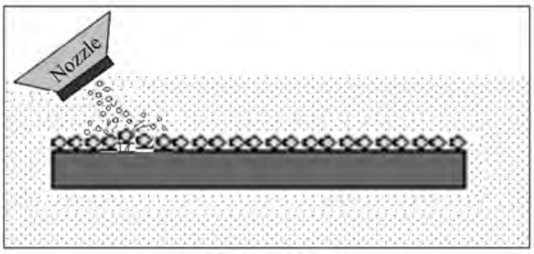
Although there are some feasible explanations for this process in earlier studies, we have another hypothesis of the mechanism of metal film stripping: the high speed fluids whose speed exceeds that of the sound may generate dramatic vibration, which decreases the adhesion between aurum and silicon substrate, and then blow off the surface of wafer by the following supersonic airstream. A schematic of this removing mechanism is shown in Fig. 7.



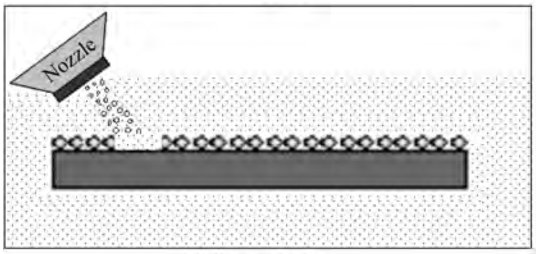
(a) Aurum coated silicon substrate



(b) Pre-stripping



(c) Stripping



(d) Post-stripping

Fig. 7. Schematic of stripping mechanism.

Besides the explanations mentioned above, which are a physical effect, we assume that there may be a chemical effect during the process. For instance, this technique may enhance the solubility of the polymer in water. Due to a loss of hydrogen bonding that occurs with decreasing density, the property of the steam-water mixture is more like a nonpolar solvent than the polar substance that is familiar under ambient conditions. In addition to density, two other key parameters that are indicators of the change in the water's property from ambient to steam are its dielectric constant and ion product or dissociation constant. The ion product and dielectric constant of high-temperature water and steam versus temperature is illustrated in Figs. 8[19] and 9[18], respectively. As shown in Fig. 10, increasing temperature will enhance the solubility of organics in water[18].

For the stripping mechanism mentioned above, we conclude that this is a complicated process including several factors and that the high temperature of the heat exchanger helps to achieve high efficiency of photoresist stripping by steam-water mixture spraying.

4. Conclusion

In this paper, we have introduced a novel photoresist stripping technology that successfully strips hard baked SU-8 photoresist without other chemicals. Though former researchers have studied and discussed the mechanism of the mixture of steam and water droplets for stripping materials, we presume that there exists some other mechanism of stripping effect and then by doing different experiments on polymer films and metal films, we find that there may also be an effect of enhancement of solubility of polymer in the cleaning process. As the steam-water mixture removes photoresist and even metal with ease and consumes water only, this process will become a potential technology for stripping applications.

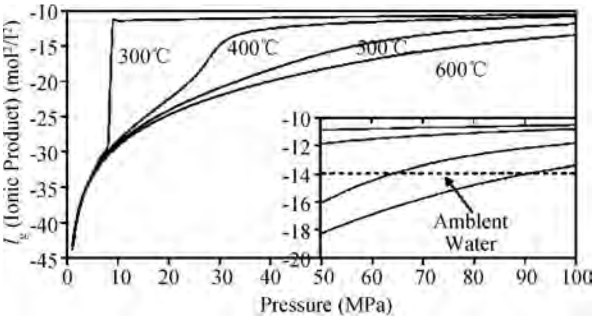


Fig. 8. Ion product of high-temperature water and steam at different temperatures versus pressure. At low pressures, water behaves as a non-polar solvent with low self-dissociation. High pressures can increase the ion product to values above those found for water at ambient conditions.

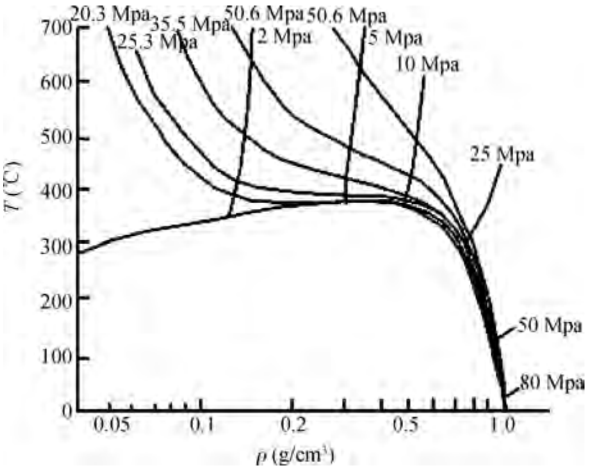


Fig. 9. Dielectric constant of water at different pressures versus density.

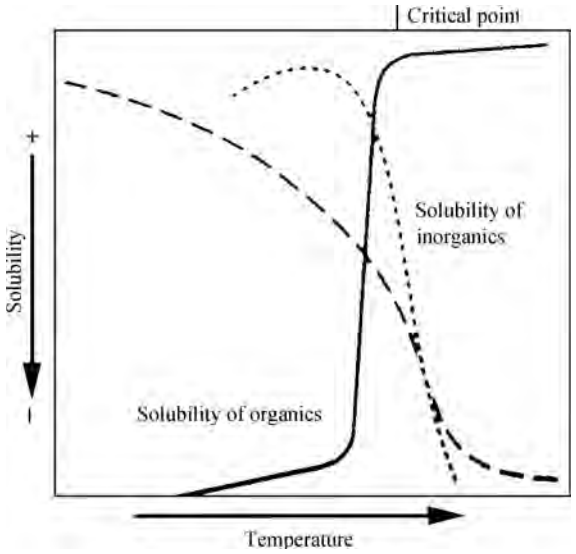


Fig. 10. Solubility of organics and inorganics in water versus temperature.

Acknowledgments

The authors thank the Integrated Circuit Advanced Process Center for equipment support.

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