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Surface modification of aluminum by toluene plasma at low-pressure and its surface properties

Youngyeon Ji*, Jeong-Hee Cho, Hee-Sun Chae

R&D center for PSK-INC Corporation, 2-12, Seoku-dong, Hwaseong-si, Gyeonggi-do 445-170, South Korea

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ABSTRACT

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Keywords: Aluminum treatment Toluene plasma Seasoning Ashing rate Non-polar surface Condition processes are commonly implemented in semiconductor fabrication to prepare plasma chamber for the optimal performance of plasma processes. When used with plasma ash and etch chambers, conditioning processes typically involve generating conditioning plasma in the plasma chamber for a predetermined length of time to prepare, or "season", the chamber for the performance of ash and etch processes with production wafers. We report on the seasoning of aluminum baffle surfaces by plasma with non-polar aromatic hydrocarbon such as toluene. The aluminum surface was simply treated by radio frequency (RF) plasma with toluene. The non-polar property of the sample increases with increasing plasma treatments. Therefore, the ashing rate of toluene coated baffle improved 1.3 times without scavenging activative species.

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1. Introduction

Plasma technology has been widely used as a surface modification method for introducing unique properties onto the surface of materials of various compositions and topographic shapes, owing to its advantage as relatively simple, fast and clean method [1-7].

One of the most useful properties of a glow discharge is that it can modify the physical, chemical and electrical properties of material surfaces. The extent of the modification is directly related to the characteristics of the boundary layer, plasma discharge parameter and plasma gas composition. In surface reaction, the three main phases are adsorption, plasma gas composition, and recombination. Adsorption is determined essentially by the nature of the excited species and by the nature of the excited atoms of the surface. The energy transfer between gas boundary layer and solid depends on the energy transfer during the desorption process. As a result of the aforementioned processes, the surfaces of material may be activated toward increased surface tension to form free radicals, ions, and exited atoms.

It is also known that bombardment of inert gas can cause different types of structural alterations on a surface. Using plasma treatment, interfacial properties can be introduced to a surface without affecting the desired bulk properties of a material such as adhesion or hydrophobicity. To prepare a plasma chamber for the optimal performance of plasma processes, condition processes are commonly implemented in semiconductor fabrication. When used with plasma ash and etch chambers, conditioning processes typically involve generating conditioning plasma in the plasma chamber for a predetermined length of time to prepare, or "season", the chamber for the performance of ash and etch processes with production wafers.

Conditioning processes may also be used to replace deposited polymeric films removed during cleaning and thus improve the initial plasma behavior in subsequent ash and etch processing. The deposited polymeric films may act as insulators, and thus can affect the coupling condition of plasmas formed therein.

Current ash and etch processes employ low pressure (about 2 torr) plasmas where the mean free path of a plasma species may be comparable to the reactor dimensions, increasing the importance of plasma-surface interactions. Plasma produced and process product species can deposit on the chamber walls during ash and etch, changing the surface reactivity for incident fluxes of ions and neutrals. Deposition of ash and etch products (or feedstock gas fragments) on the chamber walls can results in process drifts, such as changes in ash and etch rates, profiles, selectivity and uniformity during both a single ash and etch process. Pre-etch and ash plasma processes are commonly used to condition (or season) chambers to insure that they will optimally perform when the real ash process is conducted [8]. When a plasma chamber is seasoned, the chamber walls are coated, before starting to process the wafer, with a material that would otherwise be deposited in a transient manner during the course of etching and ashing. In this way, seasoning helps stabilize the actual ash and etch process by insuring that the





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^{*} Corresponding author. Tel.: +82 31 660 8898; fax: +82 31 660 0923. *E-mail address*: yy1201@psk-inc.com (Y. Ji).

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Fig. 1. A schematic illustration of the experimental setup for the RF plasma equipment.

reactor is already in a desired range of operating conditions, thus minimizing process drift and increasing the mean time between cleans. In this paper, we report on a computational investigation of the effect of seasoning of aluminum baffle for a N_2/O_2 plasma ashing of photoresist [9].

2. Experimental

The RF discharge plasma system for aluminum baffle surface treatment is shown in Fig. 1. A movable electrode was used in the present experiment for a damage free substrate. Uniform and stable plasma generation with an in reaction chamber of RF power supply was used for the experimental. An RF power electrode was connected to a 13.56 MHz RF supply through an L–C matching unit. Plasma treatment was carried out in a reactor (800 mm × 600 mm × 600 mm rectangular) connected to a rotary pump. The reactor chamber was made of aluminum.

The Toluene was bubbled by a 300 sccm argon. Toluene was then injection at approximately 50 sccm. Gas pressure is typically 300–450 mTorr at a flow rate of 200–400 sccm.

In this study, the approach consists of analyzing the gas phase as well as the surface characteristics to determine the surface chemistry, in other to be able to form a relationship between the discharge parameters and deposition properties. Therefore, we performed in situ diagnostics of a deposition system with an optical emission spectroscope (OES: Ocean Optics USB4000).

Morphological changes as a result of low-pressure plasma treatment were observed using scanning electron microscopy (SEM: JEOL JSM-6700F). The chemical functional groups of the aluminum baffle surface before and after plasma treatment were characterized by Fourier Transform Infrared (FT-IR) spectroscopy (Bruker 1FS-66/S) with a spectral resolution of 4 cm⁻¹. The surface tension components and the parameters of the raw material were calculated from the contact angle measured on the raw material surface before and after plasma treatment using deionized water. The contact angle on the raw material was measured using a sessile drop method [10] with a SEO300A (Seo Inc., Korea). In order to measure the contact angle of the raw material before and after plasma treatment, deionized water (about 5 μ l) was dropped at more than five different locations on the raw material surface at 20 °C.

3. Results and discussion

The aluminum surface was treated with toluene by low pressure RF plasma. The polarity of the aluminum surfaces were determined by measuring the contact angles of the water droplets applied onto the surfaces. Fig. 2 shows the shapes and contact angles of the water droplets placed on the aluminum samples before and after plasma treatment with the toluene precursor. The contact angles with water were measured for a drop of water (50 μ l) from a micro syringe. Before the treatment of the aluminum, the contact angles were about 57° after 1 day under atmospheric pressure. However, the contact angle of toluene treated aluminum baffle in Fig. 2 is about 91° revealing contact angles close to a hydrophobic property.





O₂N₂ plasma treatment



Octane plasma treatment Toluene plasma treatment

Fig. 2. The photograph of Shapes and contact angles of water drops placed on (a) non-treated aluminum, (b) O₂/N₂ plasma treated aluminum, (c) aliphatic hydrocarbon treated aluminum and (d) aromatic hydrocarbon treated aluminum.

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