Surface & Coatings Technology 205 (2010) 1532–1535

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

High density large area hydrogen plasma by hollow cathode plasma array

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ARTICLE INFO

Available online 26 August 2010

Keywords:
Hollow cathode
Hydrogen plasma
Photoresist stripping
Low-k dielectric films

ABSTRACT

Hydrogen plasma becomes an alternative to the conventional oxygen plasma in stripping photoresist in the next generation semiconductor processing because the conventional oxygen plasma is known to degrade ultralow dielectric constant films by depleting carbons from the films. An array of hollow cathode plasma is designed to have uniform and high density hydrogen plasma. From many combinations of cavity size and distribution, it is found that cylindrical ceramic cavity with 6 mm inner diameter, 10 mm depth and 30 mm spacing between neighboring cavities shows the widest process window. Nineteen cavities are engraved into the cathode plate of 200 mm diameter. Ceramic cavities are needed to survive against energetic ion bombardment. Dependence of the stripping rate on mixture ratio of N_2/H_2, gas flow rate, chamber pressure and RF power is investigated, and we have found that a stripping rate of more than 260 nm/min with 7% uniformity can be achieved when chamber pressure is 213 Pa, gas flow rate 10000 sccm, N_2/H_2 mixture ratio of 3:7 and RF power 2.5 KW. This high density hydrogen plasma in the order of $10^{11}/cm^3$can be a very effective method of photoresist stripping in the dual damascene process of copper metal and low-k dielectrics where oxygen plasma cannot be used.

1. Introduction

Hydrogen plasma has received more attention in next generation semiconductor processing. Especially, it has become essential in the photoresist stripping process because conventional oxygen plasma is known to degrade low-k dielectric films by reducing carbon concentration of ultralow dielectric constant materials such as SiOCH [1–5] and to cause silicon loss by forming SiO_2. It is also reported that downstream hydrogen atom and or mixture with nitrogen can minimize damage to ultra low-k dielectric materials.[1–5] However, direct plasma of hydrogen and its mixture with nitrogen can cause some property changes such as increase in k value and moisture uptake. In order to remove photoresist without seriously degrading the underlying low-k dielectric layer, downstream or remote plasma of hydrogen or nitrogen is therefore preferred. Remote plasma has been generated by placing a gap structure just above a wafer in inductively coupled plasma (ICP) [4,5] or remote microwave plasma [3]. However, it is difficult to generate high density hydrogen plasma to match the conventional oxygen plasma in the photoresist striping rate. It is easy to get a 6 μm/min removal rate at 250 °C by downstream oxygen plasma. It is reported that a removal rate of 100 nm/min was obtained by remote hydrogen discharge at 260 °C [4]. Therefore, it is required to build a downstream reactor to supply high density atomic hydrogen for faster photoresist stripping.

Hollow cathode structures to generate plasma have been used to get a high sputter deposition rate from metal targets [6,7]. An array of hollow cathode plasma (HCP) has been used to generate large area plasma for chemical vapor deposition of amorphous silicon, diamond-like carbon films,[8–11] in which applied RF power is usually less than 1 kW. In this work, an array of HCP has been designed to have a uniform and high density hydrogen plasma for photoresist stripping in the 300 mm wafer process, in which mass production environment RF power is normally larger than 2 kW. The number of hollow cavities in the cathode plate and the size of each cavity and position of baffle between the cathode and wafer stage should be optimized for high density hydrogen atom supply. Mixture ratio of hydrogen and nitrogen, gas flow rate, chamber pressure and applied RF power should also be optimized.

2. Experiment

The hollow cathode plasma (HCP) chamber consists of a cathode plate, a baffle and a wafer stage, as shown in Fig. 1. The cathode plate, whose diameter is 200 mm, has an array of cylindrical shape hollow cavities and distributed gas injection holes whose diameters are 0.4 mm. The number and size of the hollow cavities should be determined to generate HCP mode plasma in a given process condition. Process gases are fed through mass flow controllers (MFC). The baffle disc, which has many small holes of different

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doi:10.1016/j.surfcoat.2010.08.090

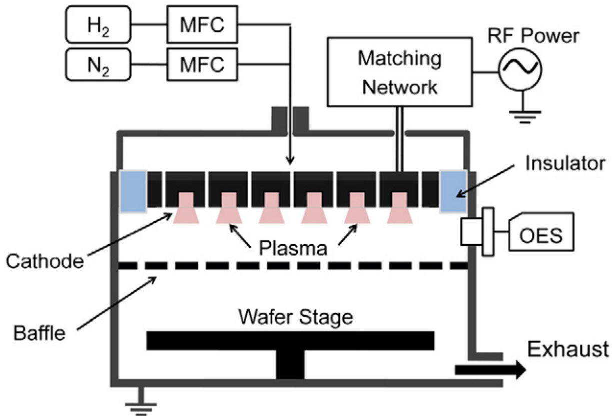

Fig. 1. Schematics of the hollow cathode plasma chamber.

sizes, is located 4 cm below the cathode and 5 cm above the wafer stage; its role is to keep ions from reaching wafers and to provide a uniform supply of atoms across wafers. It is believed that high plasma density achievable by HCP above the baffle should supply high density downstream reactive atoms to the wafer stage. The wafer stage for a 300 mm wafer is kept at 250 °C in this experiment. Chamber wall, baffle and wafer stage are made of aluminum and their surfaces are anodized. The cathode plate is also anodized; it is very important to deposit a uniform anodized layer on the cathode plate. However, it is very difficult to achieve uniform thickness especially at the edges and corners of the hollow cavities. Because high plasma potentials can be applied at these edges and corners, local arcing has been observed and plasma becomes unstable after running the photoresist stripping process for several days. In order to prevent local arcing discharge and to extend lifetime, ceramic plugs of hollow cavity shape are inserted into the hollow cavities of the cathode plate. Ceramic plugs have the shape of a cup and the thickness of the cup wall is 2 mm. The result is that the surface of the cavity is now covered by a thick insulator. The chamber is evacuated with a dry pump.

Plasma density is measured by the Langmuir probe with double probes; it is found that the electron density is on the order of $10^{11}/cm^3$ and the electron temperature is 2–3 eV. Optical emission spectroscopy is used to monitor hydrogen and nitrogen atom density. Emission intensity is converted to relative intensity using Ar actinometry. It would be more accurate to estimate the density of plasma species by monitoring Ar emission peak (750.4 nm) as a reference to compensate any change of electron energy distribution function. It is known that ratio of intensities of the reactive particle to noble atom emission can be used to monitor the relative concentration of the reactive particles as plasma parameters are varied [12]. In order to measure the stripping rate, photoresist of 193 nm photolithography is spin-coated on the 300 mm silicon wafers. Because during stripping process the wafer stage is kept at 250 °C, the photoresist gets shrunken before being fully etched. In the case of photoresist stripping by oxygen plasma, stripping rates are typically more than 6 μm/min and thus the photoresist is fully etched before getting shrunken. However, photoresist stripping by hydrogen or nitrogen plasma is too low to neglect the shrinkage rate. The shrinkage for 1 min at 250 °C is approximately 30% of the initial photoresist thickness, and thus 300 nm in thickness in the case of 1 μm thick photoresist. Therefore, shrinkage rate should be considered to calculate the real stripping rate because simple monitoring of thickness change would lead to a mistakenly large value for the stripping rate. It is reported that study on hydrogen-based remote plasma also observed photoresist thickness shrinkage [5]. The shrinkage was 300 nm/min and was described as "thermal decomposition" [5].

3. Results and discussions

In order to determine the number and size of the hollow cavities, the radius and depth of the cylindrical cavity and spacing between cavities are varied. Because the HCP mode is sensitively dependent on process conditions such as RF power, chamber pressure and processing gases, general process conditions of the photoresist stripping reaction should be set first. The hollow cathode plasma etcher will be operated in certain conditions of a mixture of hydrogen and nitrogen; of a chamber pressure higher than 70 Pa, which can be obtained by a single dry pump; and of 13.56 MHz RF power higher than 2 kW.

The inner radius of the cavities is varied at 1, 2, 3 and 5 mm; depth is varied at 8, 10, and 12 mm; and spacing is varied at 15, 20 and 30 mm. The full combination of these factors leads to too many cases to construct and evaluate, and thus the Taguchi method is employed to reduce the number of experiments [13]. The objective of this experiment is to find the cavity size and array that offers the HCP mode. There have been studies to investigate the effect of cavity depth to plasma uniformity [14] and effect of cavity distribution pattern on uniformity of deposited film [10]. When RF power is applied to the cathode, capacitively coupled plasma is generated first underneath the cathode plate, and then, if conditions are met, plasma moves into cavities and bright discharge can be observed close to the cavities.

Fig. 2 shows one aspect of many experimental results. It shows chamber pressure windows, HCP generation condition, for three different gas mixtures as a function of radius of cavity. Here, cavity depth and spacing between cavities are fixed at 10 mm and 30 mm, respectively. Chamber pressure can be allowed from 90 to 260 Pa. For a 2 mm radius cavity HCP cannot be obtained with 100% hydrogen, and for a 5 mm radius cavity HCP does not form with 100% nitrogen either. However, the mixture of hydrogen and nitrogen can provide HCP for all cavity size investigated even though the allowed chamber pressure for HCP is different from each cavity size. In order to have larger flexibility of process conditions a cavity radius of 3 mm is selected for further investigation. Plasma of either hydrogen only or nitrogen only cannot increase the removal rate and their mixture provide higher removal rate [5]. The optimized cathode plate has nineteen hollow ceramic cavities.

Optical emission spectra are collected through a quartz viewport and peaks representing nitrogen ions (peak at 391 nm) and hydrogen atoms (peak at 656 nm) and argon atoms (peak at 750 nm) for Ar actinometry are monitored. Their intensities are collected as a function of the H_2/N_2 mixture. Ar emission intensity increases as the H_2 content increases, which indicates increasing excitation efficiency of Ar, which is again related to electron energy distribution [12]. It is known that the ratio of

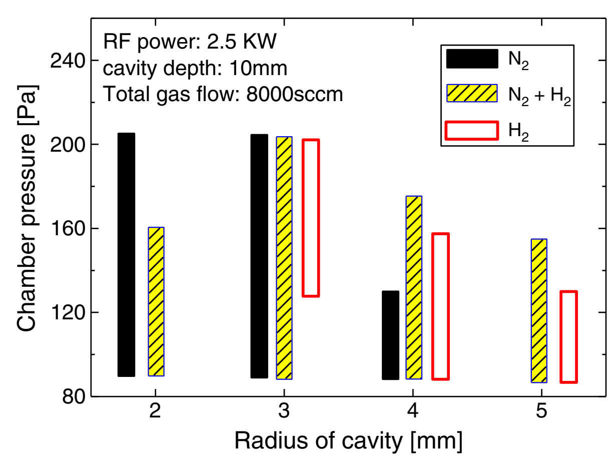

Fig. 2. Process windows of possible hollow cathode plasma in terms of the cavity radius for three different gas mixtures. Bar means hollow cathode plasma generation.