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Stripping of photoresist using a remote thermal Ar/O₂ and Ar/N₂/O₂ plasma

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Photoresist is etched using a remote thermal (cascaded arc) plasma in Ar/O₂ and Ar/O₂N₂ mixtures. Very high etch rates, up to 200 nm/s, are achieved at low substrate temperatures (350 K) and low electron and ion temperatures (<0.5 eV). The addition of small amounts of nitrogen (3%) leads to an increase in etch rate. The etch rate in Ar/O₂/N₂ also increases with time during the etching process. The details of the plasma and surface chemistries are not yet well understood. © 2003 American Vacuum Society. [DOI: 10.1116/1.1532021]

I. INTRODUCTION

One of the most frequently recurring steps in the processing of wafers in the semiconductor industry is the postetch cleaning of the wafers. After a photoresist layer has been applied, exposed to (UV) light and etched, the residual photoresist has to be removed along with other etch residues. Traditionally, this is done by wet chemical etching. With the use of new materials and ever-smaller feature sizes came the need for more selective and controllable cleaning techniques. Since the 1980s, dry plasma etching is being applied for the removal of photoresist.¹ At first, rf (13.56 MHz) plasma processing was applied, in which the wafers are directly exposed to the plasma. With a plasma system it was possible to remove more complex photoresist materials and other residues. An added advantage is the elimination of toxic chemicals. A disadvantage of such a system is the occurrence of large bias potentials and charging of the wafers in a rf discharge. Ions are accelerated by the bias potential, which leads to ion bombardment causing damage at the surface. Current induced in the wafers due to charging of the wafers may cause breakdown of underlying components inside the wafer. Since the beginning of the 1990s, downstream microwave processing^{2,3} is the technology of choice. The plasma is created in a microwave cavity but the actual etching process takes place downstream from the source. This reduces the bias potential of the wafer and the damage from ion impact. The plasma creates mainly neutral oxygen atoms needed for the removal of the photoresist. With a remote system it also became possible to move from batch processes (in which a batch of wafers is placed inside the plasma) to continuous, single wafer processes. Furthermore, reactive gases, such as fluorine, can be added to the plasma outside the source, with-

out the risk of damaging the plasma source. It appears that remote plasma processing is the most promising technology for the removal of photoresist and other residues. From the experience with downstream microwave processing the demands of a plasma cleaning system can be summarized in four requirements:

- (1) The ability to remove a wide variety of substances by the use of different gas compositions.
- (2) The ability to use the tool in a continuous process.
- (3) Low bias potential to prevent damage.
- (4) High radical density to reduce processing times.

In this context, the use of a dc arc (cascaded arc) source is investigated here for its use in the removal of photoresist. It has many of the same features as a downstream microwave system, but produces radicals at a much higher intensity.⁴ This should lead to higher rates of removal of photoresist. The charge exchange and dissociative recombination^{5,6} reduce the amount of ions in the plasma and create reactive atoms. The improved ratio between atoms and ions means that the flux of ions is relatively small and with that, the current through the wafers. The supersonic expansion also makes this source truly remote in the sense that there is no influence of the downstream plasma conditions on the source. By changing downstream conditions such as background pressure, the density of the reactive particles can be influenced. In addition, a direct current source such as the cascaded arc is easier to use since it does not need the (constant) tuning of a microwave system.

Since plasma induced damage is always a matter of concern in plasma processing, independent tests (high-frequency CV and charge-to-breakdown measurements) were commissioned at the Interuniversity Microelectronics Center, Leuven, Belgium (IMEC) to investigate possible plasma process

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FIG. 1. Remote thermal arc for deposition and etching. The plasma source is a six plate cascaded arc.

induced damage to the wafers. No damage was noticeable in the stripped wafers.⁷

II. EXPERIMENTAL SETUP

The experimental setup used in these experiments is the expanding arc setup. The setup is shown schematically in Fig. 1 and extensively described in Refs. 8–10. The source is a cascaded arc source with six copper cascade plates with an internal bore of 4 mm diam. A current of 82 A is drawn from three cathodes to the anode plate. Inside the arc the pressure is subatmospheric (0.1–1 bar), the electron temperature is approximately 1 eV, and the electron density is high (10^{21} – 10^{22} m⁻³). In the anode plate a nozzle is mounted through which the plasma is allowed to expand supersonically into the low-pressure chamber (1–500 Pa).¹¹ Here, the electron temperature is low (0.1–0.3 eV) and the electron density is of the order 10^{16} – 10^{19} m⁻³ depending on the position in the plasma and gas composition, as will be discussed later. The source is movable along the vertical axis of the chamber. Inside the vessel is a substrate holder with temperature control and cooled with liquid nitrogen. Samples are

TABLE I. Standard operating conditions.

Ar flow	60 sccs
O ₂ flow	0–17 sccs
Arc current (I_{arc})	82 A
Chamber pressure	3 mbar
distance arc–substrate	30 cm
substrate temperature	350 K

clamped down mechanically on the substrate holder. A small back flow of helium ensures good thermal contact between the sample and holder.¹²

Argon and nitrogen are injected into the arc at the cathode side of the arc. Oxygen is injected in a ring inside the vessel, 4 cm downstream from the nozzle. In some of the experiments oxygen was also injected directly into the nozzle and into the arc through a channel in the last plate. Because of concern about possible wear to the arc source this last injection method was only applied in two experiments. In the experiments described here, a standard condition was chosen around which different parameters were varied. These standard conditions are summarized in Table I.

The photoresist (Sumitomo PFI 38A) was spin coated on 6 in. silicon wafers supplied at IMEC Leuven. The resist was baked at 423 K (150 °C). The wafers were cut into smaller, 2×2 cm samples that can be clamped onto the substrate holder. The resist layer has a thickness of 1.2 μ m and a refractive index of 1.62. The thickness of the layer and etch rates are determined using *in situ* ellipsometry. The measured ellipsometric angles, Ψ and Δ , are simulated to obtain thickness, etch rate, and refractive index.¹³ An example is shown in Fig. 2.

III. THEORY

For the removal of photoresist by plasma treatment it is generally acknowledged that oxygen atoms are the etching species.^{14–17} In the investigation of the downstream arc plasma as a source of atomic oxygen, argon is used as the carrier gas that is activated in the arc. Argon ions emanate from the arc and oxygen gas is injected into the stream 4 cm from the nozzle. Generation of oxygen takes place by charge exchange and dissociative recombination (see, for example, Refs. 4, 5, and 18):

FIG. 2. Ellipsometry measurements during photoresist stripping. (a) Curves in a Ψ – Δ plot. (b) Ψ as a function of time. The solid lines are simulations with a refractive index $n = 1.62$.

The charge exchange reaction is exothermic (the ionization energy for O_2 is 12.06 eV, for Ar it is 15.6 eV) with a rate of approximately $10^{-16} \text{ m}^3 \text{ s}^{-1}$.¹⁹ The rate for dissociative recombination is of the order $10^{-13} \text{ m}^3 \text{ s}^{-1}$.²⁰ After dissociation, the oxygen atoms are transported further downstream to where the substrate is positioned.

It is clear already from this simple kinetic model that the amount of oxygen atoms produced is limited by the amount of argon ions produced inside the arc. To enhance the production of oxygen atoms, nitrogen is added to the argon as a carrier gas. Similar to the situation with argon, nitrogen ions will undergo charge exchange and dissociative recombination with the oxygen molecules injected downstream. In addition, neutral nitrogen atoms are produced in the thermal arc plasma where the dissociation degree is close to 100% due to the high electron density and temperature inside the arc.²¹ These nitrogen atoms will react with the oxygen molecules in the downstream plasma to form nitric oxide and additional oxygen atoms.^{22,23}

The rate for this reaction is approximately $5 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$.²² The nitric oxide can react with nitrogen atoms to form another oxygen atom:

with a rate of $10^{-16} \text{ m}^3 \text{ s}^{-1}$.²² In principle, both reactions [Eqs. (2) and (3)] are reversible so that also the back reaction will take place. However, both reactions are exothermic in the direction indicated, yielding 1.4 and 3.2 eV for Eqs. (2) and (3), respectively. This means that for the backward reactions activation energy is required. Since the temperature of the downstream plasma is much lower [approximately 0.3 eV (Ref. 9)], the corresponding reaction rates will be small. The main result will be additional production of oxygen atoms through reactions (2) and (3) when argon/nitrogen is used as the carrier gas, compared to the pure argon plasma.

IV. RESULTS

A. Argon/oxygen

1. Substrate temperature

The etching rate depends mainly on the flux of atomic oxygen at the substrate and the etching reaction rate constant. The latter depends on the substrate temperature and the activation energy of the surface reaction, E_a . If linear kinetics are assumed for the reaction at the substrate, the reaction rate, R_s , can be expressed by

$$R_s = R_{s0} e^{-E_a/kT_s}. \quad (4)$$

The etching rate is shown in an Arrhenius plot as a function of reciprocal substrate temperature in Fig. 3 (squares). The plasma conditions were kept constant, so that the oxygen flux at the substrate is constant. The activation energy is

FIG. 3. Etch rate as a function of reciprocal temperature; ■ oxygen/argon, and ▲ oxygen/nitrogen/argon plasma mixture. Solid lines are linear fits to the data below 423 K.

fitted to the measurements at temperatures below 400 K. The activation energy found is $5 \pm 1 \times 10^{-21} \text{ J/K}$, the equivalent of $250 \pm 50 \text{ K}$. The data above a substrate temperature of 400 K deviate strongly from the line fitted. This is due to the fact that the photoresist was baked at 423 K. When the samples are heated above this temperature, structural changes in the photoresist start taking place, even before the plasma etching has started. For this reason, further experiments have been performed at a substrate temperature of 350 K.

2. Oxygen flow rate and pressure

Figure 4 shows the etch rate as a function of oxygen flow rate at different background pressures (25, 100, and 300 Pa). The argon flow rate and current through the arc have been kept constant. In very general terms, an increase of the pressure will decrease the mean-free path and lower the diffusion (of argon ions and oxygen atoms) towards the vessel walls, and thus increase the etch rate at the position of the sample. Increasing the oxygen flow rate will increase the production of oxygen atoms. Since the flux of argon ions is limited, it is to be expected that at high oxygen flow rate the etch rate will tend to a limit. This limit is reached when all argon ions have reacted with oxygen molecules following Eq. (1). Then, the flux of oxygen atoms equals twice the flux of argon ions emanating from the arc. The ionization degree inside the arc is approximately 10%.^{9,11} With an argon flow rate of 60 sccs,

FIG. 4. Etch rate as a function of oxygen flow rates at different background pressures: ♦ 300 Pa, ▼ 100 Pa, and ■ 25 Pa.

FIG. 5. Comparison of the etch rate using different injection methods. (a) 300 Pa background pressure, $\blacklozenge$ ring injection (as in Fig. 4), and $\diamond$ nozzle injection. (b) 25 Pa, $\blacksquare$ ring injection and $\square$ injection into the arc channel.

the ion flow from the arc is estimated to be 6 sccs. Indeed, for low oxygen flow rates an increase in the etch rate is observed with an increase of oxygen flow. Also, the etch rate increases with increased background pressure, as expected.

Rather surprising is the observation that at higher oxygen flow rates (>3 sccs) the etch rate decreases and tends to a lower limit. Loss of oxygen atoms in the gas phase is not expected. Ozone formation ($O + O_2 + O_2 \rightarrow O_3 + O_2$) or association of atoms ($O + O + O_2 \rightarrow 2O_2$) is negligible at these pressures. The (qualitative) explanation for the decrease in etch rate could come from the realization that oxygen atoms can diffuse faster than the argon ions. At high oxygen flow rates the partial pressure of O_2 increases and Eq. (1) becomes faster. Consequently, the argon ion density decreases more quickly as a function of distance from the nozzle due to the reaction with oxygen molecules, and most of the atomic oxygen will be formed close to the nozzle. In this case the oxygen atoms will have more time to diffuse and be lost at the vessel walls before they reach the sample position, so that the eventual density at the position of the sample will be lower. For a complete quantitative analysis, a complete numerical model of the plasma including the flow in front of the substrate and the reactions taking place at the surface is needed.

3. Injection method

In the setup used, different methods are available for the injection of oxygen into the argon plasma. In the previous results oxygen was injected through a ring, 4 cm downstream from the nozzle. Other positions where oxygen can be injected are injection into the nozzle and injection through the last plate of the cascaded arc into the arc channel. In Fig. 5(a), the effect of injection into the expansion nozzle on the etch rate is compared to injection through the ring. No significant changes in etch rate are observed.

A different situation occurs when oxygen is injected through the last plate of the cascaded arc, directly into the arc channel. Inside the arc the electron density and temperature are high ($>10^{20} \text{ m}^{-3}$ and 1 eV, respectively). This enables extra dissociation mechanisms for the oxygen molecules by electron impact and by thermal dissociation:

and

The etch rates obtained when oxygen is injected into the arc are compared to ring injection in Fig. 5(b). When a small amount of oxygen is injected, the increase in etch rate is small. In this case, the extra production through Eqs. (5) and (6) is negligible compared to the oxygen produced by the argon ions [Eq. (1)]. When larger amounts of oxygen are injected an enhancement of the etch rate is observed of up to a factor 2. Because of fear of extensive wear to the arc, no further investigation of the etching behavior was undertaken with oxygen injection into the arc channel.

B. Argon/nitrogen/oxygen

In the remote thermal argon/oxygen plasma with injection through the ring or in the nozzle, the production of oxygen atoms is limited by the amount of argon ions coming from the plasma source [Eq. (1)]. To overcome this limitation nitrogen was added to the argon as the carrier gas. Due to the high electron density and temperature inside the arc, the dissociation degree will be high (up to 100% of the N_2 flow added⁴). The nitrogen atoms can dissociate the oxygen molecules injected downstream according to Eq. (2). Higher etch rates are, therefore, expected when an argon/nitrogen mixture is used as the carrier gas. The etch rate was determined as a function of oxygen flow at different partial flows of nitrogen in argon. The results are shown in Fig. 6(a). The total flow of the carrier gas (argon+nitrogen) was kept constant at 60 sccs. The background gas was fixed at 300 Pa, the substrate temperature at 350 K, and the oxygen was injected through the ring. The data at 0% nitrogen are the same as shown in Figs. 4 and 5(a) and are shown again for comparison.

When nitrogen is added to the carrier gas the etch rate increases, as expected. Moreover, the etch rates do not decrease after reaching their maximum value, as was the case in the argon/oxygen plasma. This is a very interesting result in itself, since it makes the etch rate less critically dependent on the oxygen flow rate, which makes tuning the plasma and processing times easier. Although the general behavior (the increase in etch rate when nitrogen is added) can be explained using Eq. (2), the exact dependency of etch rate on the nitrogen admixture is puzzling. The same data as in Fig. 6(a) are shown in Fig. 6(b) but plotted as a function of ni-

FIG. 6. (a) Etch rate as a function of oxygen flow rate at different nitrogen seeding percentages. $\diamond$ 0%, $\triangle$ 3%, $\bullet$ 8%, and $\blacksquare$ 50%. (b) Etch rate as a function of nitrogen seeding percentages at different oxygen flow rates. $\blacksquare$ 3 sccs oxygen, $\bullet$ 5 sccs, $\triangle$ 10 sccs, ∇ 13 sccs, and $\diamond$ 17 sccs.

trogen percentage. Figure 6(b) shows more clearly that just a small addition of nitrogen increases the etch rate considerably. A higher percentage of nitrogen only slightly increases the etch rate further. This is not according to the expected behavior based on Eq. (2). From Eq. (2) alone, one would expect a gradual increase of the etch rate with nitrogen percentage, as the amount of nitrogen atoms produced increases with the nitrogen flow rate. Another observation made is shown in Fig. 7. In Fig. 7 the etch rate is shown as a function of time at different nitrogen seeding percentages (Fig. 6 shows the time averaged etch rates). In the case that only argon is used as the carrier gas, the etch rate remains constant in time. But when an argon/nitrogen mixture is used, the etch rate increases with time during the etching process. Since no changes in the plasma were observed in time, the increase in the etch rate suggests some surface process (the substrate surface changes in time, because it is etched). Figure 7 also shows that this increase in etch rate with time does not depend significantly on the amount of nitrogen. Even at 3% nitrogen the increase in the etch rate is observed. These two observations cannot yet be explained satisfactory.

V. CONCLUSIONS

Very high etch rates were achieved (up to 200 nm/s) using the expanding thermal arc plasma. These etch rates are approximately 10–100 times higher than observed in remote microwave plasmas at similar background pressure and substrate temperatures.^{2,3} The etch rate increases with back-

FIG. 7. Etch rate as function of time at different nitrogen seeding percentages. $\diamond$ 0%, $\triangle$ 3%, $\bullet$ 8%, and $\blacksquare$ 50%.

ground pressure, as expected. When using argon as the carrier gas and injecting oxygen downstream through the ring, the etch rate initially increases with oxygen flow rate. At higher oxygen flow rates (>3 sccs) the etch rate decreases. Injecting oxygen in the nozzle of the source does not change the etch rate. Injection of oxygen directly into the arc increases the etch rate at high oxygen flow rates due to the dissociation of oxygen molecules by electron impact in the arc.

Adding a small amount (3%) of nitrogen to argon as the carrier gas results in higher etch rates. The etch rate does not decrease at high oxygen flow rates. Adding more nitrogen does not lead to much higher etch rates. An increase of the etch rate as a function of time was observed in the argon/nitrogen/oxygen plasma. This may suggest a surface process induced by the presence of nitrogen.

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