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Influence of the ion bombardment of O_2 plasmas on low-k materials

Patrick Verdonck [a,*], Vladimir Šamara [a,b], Alec Goodyear [b], Abdelkarim Ferchichi [a], Els Van Besien [a], Mikhail R. Baklanov [a], Nicholas Braithwaite [c]

[a] IMEC, Kapeldreef 75, 3001 Leuven, Belgium
[b] The Open University, Materials Engineering, Walton Hall, Milton Keynes MK7 6AA, UK
[c] The Open University, Department of Physics and Astronomy, Walton Hall, Milton Keynes MK7 6AA, UK

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ABSTRACT

In this study, special tests were devised in order to investigate the influence of ion bombardment on the damage induced in low-k dielectrics by oxygen plasmas. By placing a sample that suffered a lot of ion bombardment and one which suffered little ion bombardment simultaneously in the same plasma, it was possible to verify that ion bombardment in fact helped to protect the low-k film against oxygen plasma induced damage. Exhaustive analyses (ellipsometry, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, porosimetry, capacitance–voltage (C–V) measurements, water contact angle analysis) show that ion bombardment induced the formation of a denser top layer in the film, which then hampered further penetration of active oxygen species deeper into the bulk. This was further confirmed by other tests combining capacitively and inductively coupled plasmas. Therefore, it was possible to conclude that, at least for these plasmas, ion bombardment may help to reduce plasma induced damage to low-k materials.

1. Introduction

Low-k materials are used to decrease the parasitic capacitance between the metal tracks on integrated circuits and so to increase the speed of signal propagation across a device. There are various ways to make low-k materials, but their integration into single and double damascene schemes has proved to be more difficult than initially envisaged. Several processes and steps such as etching, resist stripping and chemical mechanical polishing may induce such severe damage to a low-k film that the final result is unacceptable. Understanding the damage mechanisms is one of the key factors for successful integration [1–3]. Metal liner depositions and copper reduction plasmas may also have detrimental effects [4,5]. Ion bombardment has been mentioned as one of the causes of damage of the low-k material [4].

Although the effects of several plasma treatments on low-k films are documented, the exact mechanisms are not yet completely understood. Better understanding of the interplay between plasma chemistry and physical ion bombardment, and the resultant effect on surface modification, is required. In the case of oxygen plasmas, which are used to strip the resist, the following general mechanisms have been proposed. The oxygen atoms react with and remove the CH_x groups in the low-k material film. This CH_x removal has several effects: the film becomes denser and less hydrophobic, so more water is absorbed and the permittivity increases. Physical ion bombardment can also densify the film [6–9]. However, it is not clear whether or not ion bombardment tends to increase the induced damage. Recent research has shown that the most important species in oxygen plasma are the active O species [7,8] and that inductively coupled plasmas in oxygen induced more damage than a combination of inductive and capacitive oxygen plasmas [10].

A technique that uses two identical samples in the same plasma, one on a powered electrode and the other at floating potential on an insulating ceramic post, has been previously demonstrated to be an effective way to isolate the influence of ion bombardment from chemical plasma etching. Ion bombardment is shown to be a very important factor for silicon etching, even in the lateral etching direction [11]. In this work, the same technique is used in conjunction with a mixture of capacitive (CCP) and inductive (ICP) sources in order to elucidate the role of the ion bombardment in inducing damage in low-k films.

2. Experimental details

Fig. 1 shows the schematic of the experimental setup. The plasma treatments were performed in an Oxford Instruments Plasma Technologies PlasmaLab80+, a compact plasma reactor, where it is possible to apply power to the lower electrode (CCP) and/or to the upper coil (ICP). Most experiments were performed in pure oxygen though in some cases pure argon was used instead. The gas pressure was maintained at 13 Pa; at this pressure the ion transit across the sheath is unlikely to be entirely collision-free. The power level in the CCP

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[*] Corresponding author. Tel.: +32 16 287658.
E-mail address: verdonck@imec.be (P. Verdonck).

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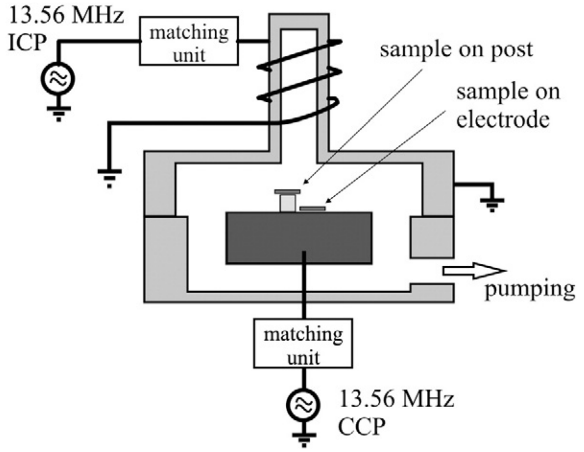

Fig. 1. Schematic drawing of the experimental set-up.

mode was 100 W or 300 W but in the ICP it was 500 W. A ceramic post of 15 mm diameter and 15 mm height was placed on the powered electrode and samples were placed on top of this post and directly, but not clamped, on the electrode surface. The plasma sheath thickness for these conditions is of the order of a few mm and conforms to the profile of the post. The capacitance of the sample on top of the post was sufficiently small so that its surface was at the DC floating potential (V_f) with respect to the plasma and therefore ions reached the sample with an energy up to around 20 eV. On the other hand in CCP mode the sample placed directly on the lower electrode was bombarded by ions that have a much higher energy, corresponding with up to the full RF induced self-bias voltage (of several hundreds of volts) plus the plasma potential. Based on the self-bias of the powered electrode, the typical ion energy for the 100 W CCP conditions was 300 eV and at 300 W was up to 470 eV. For the ICP plasmas, the ion energy on both samples is of the same order of magnitude, as when there is no bias voltage applied to the lower electrode. Employing Child's law and assuming a voltage of 300 V, an electron temperature of 3 eV and an electron density of 10^{10} cm^{-3}, one calculates a sheath thickness of 3.2 mm. This is compatible with visual observation of the sheath for these plasmas [12]. Hence the post is much higher than this sheath. Moreover, the height of the post is such that the RF impedance it presents to the applied RF voltage prevents the sheath over its top surface from developing significant self-bias.

It is important to note that the fluxes of chemical species, of photons and also of the ions were (approximately) the same at both sample locations. When exposed to a pure CCP, the only significant difference between the conditions experienced by the two samples was the energy of the incoming ions. There is a difference of temperature between the samples on the electrode and those on the post, as there is a slightly better cooling on the electrode than on the post. Temperature measurements were done on a similar reactor for a similar CCP plasma and there the temperatures could be estimated to be approximately 120 °C on the electrode and 180 °C on the post. This is still substantially cooler than the deposition and curing temperatures of the low-k films of respectively 300 °C and 430 °C.

The test samples comprised standard silicon substrates with 170 nm films of porous low-k material comprising SiCOH. This film was formed from a plasma enhanced chemical vapour co-deposition of the matrix material and the porogen that was then cured in UV light to remove the porogens, creating a porous film. The UV cure also improved the mechanical characteristics of the film. The thickness of the low-k film before and after plasma treatment was measured by ellipsometry and a toluene-take-up method was used to quantify porosity. The relative permittivity constant (*k*-value) was measured by capacitance–voltage (C–V) measurements using different Pt dots in a range from 300 to 500 μm diameter, and a continuous Pt film at the back side, with correction for all parasitic capacitances and verifying possible frequency effects. The average of at least 6 measurements was taken. The surfaces of the low-k film were characterised by water contact angle (WCA), taking the average of 5 measurements. The bulk was analysed in terms of Fourier transform infrared (FTIR) spectroscopy spectra with measurements based on averaging 64 spectra over the range 400 cm^{-1} to 4000 cm^{-1}, with a resolution better than 1 cm^{-1}. The chemical composition of the film as a function of depth was determined by X-ray photoelectron spectroscopy (XPS).

The original films had a dielectric constant of 2.3, porosity of 28% and an average pore radius of 0.8 nm. They were hydrophobic, with a water contact angle (WCA) of more than 90° and FTIR spectra showed no features characteristic of water in the region from 3000 cm^{-1} to 3500 cm^{-1}. The XPS analysis showed a composition of 33% of Si, 33% of O and 34% of C—with XPS it is not possible to measure the H content.

3. Results and discussion

3.1. Results of the first test series

The first test was a comparison of films placed on the electrode and on the ceramic post during a 5 minute exposure to a 13 Pa, 100 W CCP O_2 plasma.

The thickness of the low-k film was reduced for both samples: the sample on the post was reduced by approximately 41 nm, almost twice that for the sample on the electrode (approximately 21 nm reduction). The WCA decreased to 63° for the sample on the electrode and to 51° for the sample on the post, showing a higher hydrophilicity for the sample treated at the post than for the one on the electrode.

The XPS analyses of both samples are shown in Figs. 2A (sample on post) and B (sample on electrode) and in Table 1. Fig. 2A shows that the chemical composition was very uniform over the complete depth for the sample of the post. The oxygen had apparently penetrated throughout the complete film and removed most of the carbon leaving a film comprising SiO_2. Fig. 2B shows that the sample on the electrode was transformed in a quite different way. At the surface and top quarter (approximately 40 nm) of the film, the film composition was approximately the same as for the sample on the post. However, deeper in the film, the oxygen concentration was lower and as well as SiO_2, SiO also could be found in the film. Near the dielectric-silicon interface, the chemical composition of this film was not very different from the pristine material. Numbers indicating the relative concentration of Si, O and C are given in Table 1.

There was also a huge difference for the FTIR analyses. The oxygen plasma decreased the CH_3 content of the film and increased the water content, but there were marked differences depending upon the location of the sample. The amplitude of the CH_3 peak at 2980 cm^{-1} was decreased twice as much for the sample on the post than for the sample on the electrode. The decrease for the Si-CH_3 peak at 1280 cm^{-1} was 2.5 times larger, as shown in Fig. 3. This same figure shows also that a part of the Si—O bonds have changed: the peak of the convolution of the different Si—O bonds moves to higher wave numbers; this is a clear indication that some of the suboxide bonds (peak at around 1035 cm^{-1}) are transformed into network Si—O bonds (peak at around 1065 cm^{-1}) [13]. This transformation again is much more outspoken for the sample on the post than for the sample on the electrode. The water peak in the 3000–3500 cm^{-1} range had increased 1.8 times more for the sample on the post than for the sample on the electrode, as shown in Fig. 4. This FTIR analysis again is a very clear indication that the chemical structure of the film was modified much more for the sample on the post than for the sample on the electrode.

The ellipsometric porosimetry analyses give a strong indication how these (somewhat unexpected) results might be explained. For