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$CoSi_x$ contact resistance after etching and ashing plasma exposure

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The authors investigated the contact resistance fluctuation caused by $CoSi_x$ damage in plasma etching and ashing processes. They found that $CoSi_x$ layers damaged by plasma process exposure are readily oxidized when exposed to air resulting in increased resistance. They also found that the contact resistance increases more when CH_3F is used instead of CF_4 during etching process. The lower the mass number of dominant ions becomes, the deeper the ions penetrate. Molecular dynamics simulation revealed that dissociated species from lighter ions penetrate deeper and that this stimulates deeper oxidation. They also found that contact resistance further increased by using postetch ashing plasma even in an H_2/N_2 ashing process in which O_2 was not used. Here, too, the reason for this is that the ion penetration causes deep oxidation. They observed that the contact resistance has a linear relationship with the oxide concentration in $CoSi_x$. This leads to the conclusion that it is essential to precisely control the ion energy as well as to properly select the ion species in the plasma process in the fabrication of next-generation semiconductor devices. © *2009 American Vacuum Society.* [DOI: 10.1116/1.3130146]

I. INTRODUCTION

Silicidation of the source/drain is required to produce high-speed complementary metal oxide semiconductor devices. Selective etching of dielectric films over $CoSi_x$ layer using fluorocarbon plasma has previously been achieved due to the low volatility of cobalt fluorides in the films. In doing so, however, the $CoSi_x$ layers were damaged during the etching and ashing processes, and this resulted in contact resistance fluctuation.

In addition to contact resistance, another important issue to address in stabilizing transistor properties is how to suppress the damage caused by plasma processing. Thus, considerable discussion has been devoted to topics such as how to control plasma damage[1,2] and how to create models for controlling surface reaction during the plasma etching processes.[3–5]

To achieve stable contact resistance, it is essential to precisely control both the silicide conditions and the plasma damage. In recent years, therefore, many studies reported on the formation of silicidation[6] or on postetching processes that can suppress oxidation on silicide.

It has been reported that *in situ* nitrogen plasma treatment after etching decreases the amount of remaining fluorine and suppresses the degree to which nickel silicide ($NiSi_x$) is oxidized when it is exposed to air.[7] It has also been reported that chemical dry cleaning before metallization is an effective way to remove oxidized layers and maintain low stable contact resistance.[8] In this study, we investigated the mechanism of fluctuation in contact resistance caused by plasma processes.

II. EXPERIMENT

For our experiments, we used a $SiO_2/SiN/CoSi_x$ stacked samples with hole patterns (Fig. 1). We investigated the re-

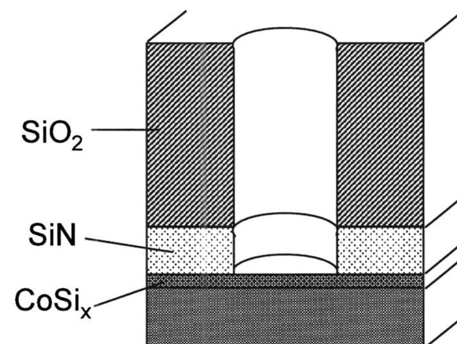

FIG. 1. Schematic cross-sectional view of contact sample.

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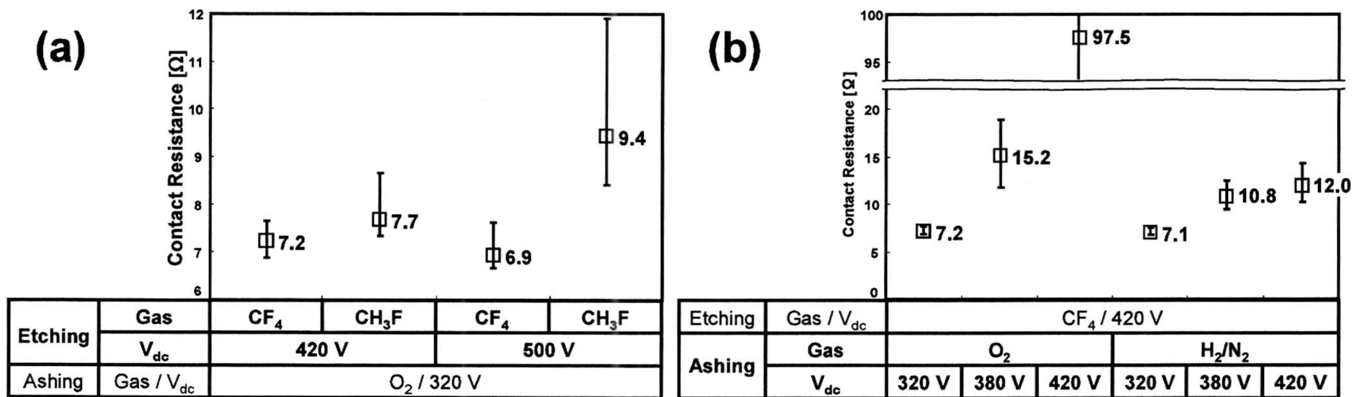

FIG. 2. Contact resistance dependence on (a) etching and (b) ashing conditions.

lationship between the plasma parameters and the contact resistance to $CoSi_x$ using a dual-frequency (27/2 MHz) capacitively coupled plasma system. The gap between the two electrodes was fixed at 23.5 mm. The temperatures of the top and bottom electrodes were kept at 80 and 35 °C, respectively. We used CF_4/Ar or CH_3F/Ar plasma for SiN etching (V_{dc}=420–500 V), and the O_2 or H_2/N_2 plasma (V_{dc} =320–420 V) for the subsequent ashing process. The pressure was fixed at 50 mTorr in each plasma process. In SiN etching, we fixed the Ar flow rate [300 SCCM (SCCM denotes cubic centimeters per minute at STP)] and adjusted the CF_4 or CH_3F flow rates to prevent the CF polymer from depositing on the substrate. Wet cleaning was carried out within 12 h after plasma processes. After that, we measured the ϕ0.23 μm Kelvin contact resistance (16 points in each wafer) that was exposed to each set of plasma conditions. The thickness and the composition of the damaged layer were analyzed using x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and transmission electron microscopy (TEM). SIMS and XPS were measured after sufficient time of air exposure in order to compare the steady-state surface conditions. The ion energy distribution function (IEDF) and the ion penetration depth were calculated using Monte Carlo simulation and molecular dynamics (MD) simulation,[9] respectively.

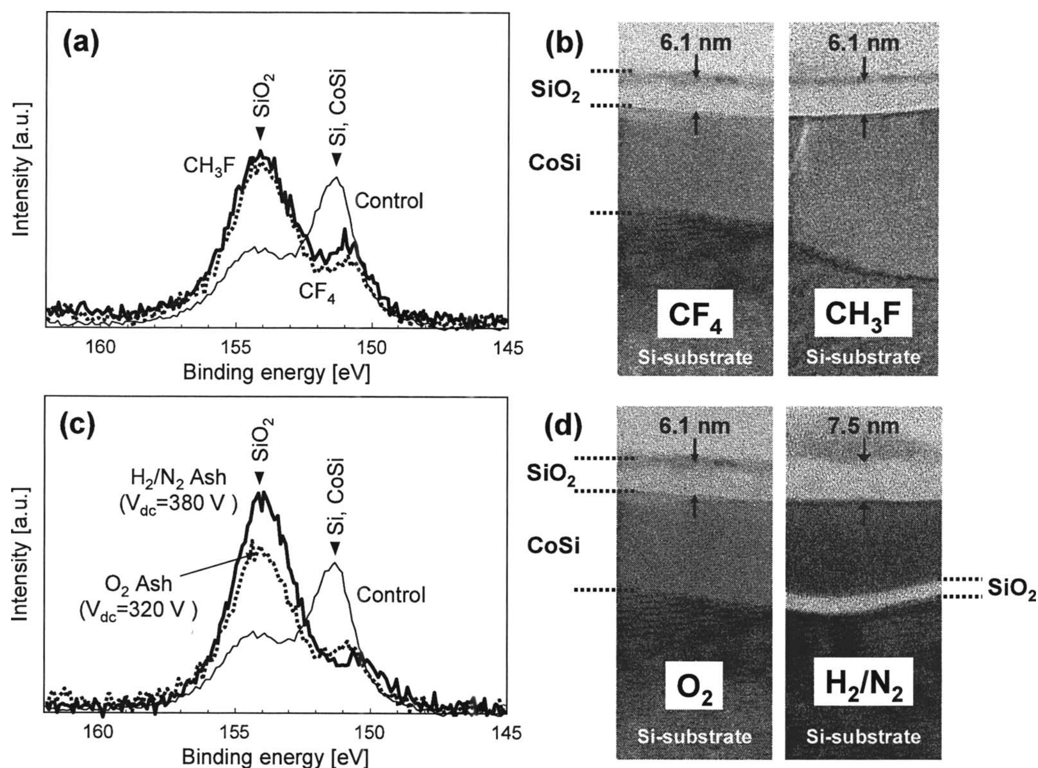

FIG. 3. XPS spectra [(a) and (c)] and TEM image of $CoSi_x$ [(b) and (d)] in samples exposed to each set of plasma conditions. [(a) and (b)] Comparison of CH_xF_y etching plasma conditions. [(c) and (d)] Comparison between O_2 and high V_{dc} content H_2/N_2 ashing plasma condition.

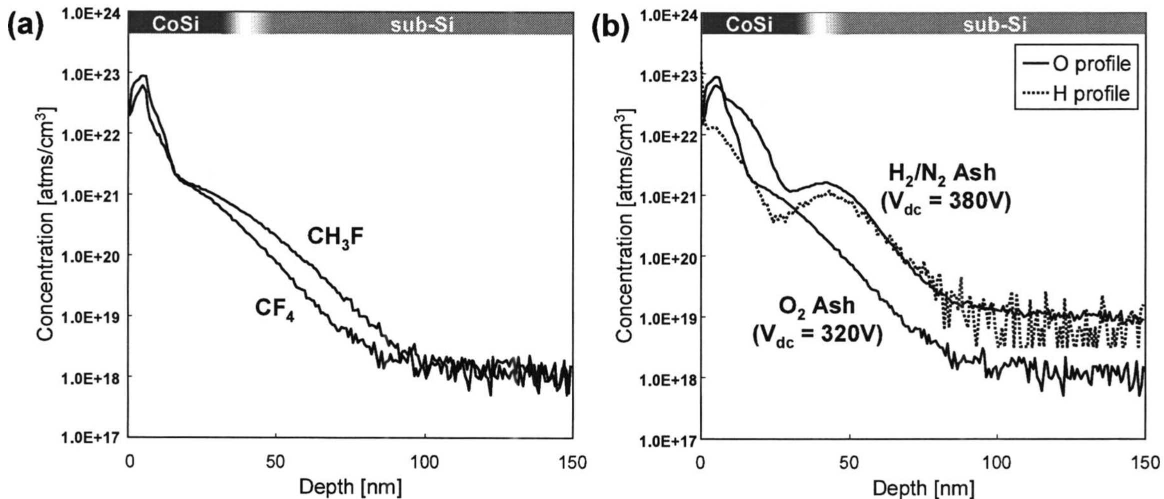

FIG. 4. Depth profiles of O and H concentration of CoSi$_x$ in samples exposed to etching and ashing plasma. (a) Dependence on etching gas at V_{dc}=420 V and (b) under ashing condition.

III. RESULTS

A. Contact resistance versus etching gas (CH$_x$F$_y$) composition

We used CH$_x$F$_y$ plasma etching to fabricate the contact to CoSi$_x$. The contact resistance that was exposed to each set of plasma conditions is shown in Fig. 2(a). The contact resistance increased more when CH$_3$F was used than when CF$_4$ was used and a further increase was observed when the amount of V_{dc} in CH$_3$F was high. The results we obtained showed that the contact resistance differed depending on the gas species used; this point will be discussed later.

B. Contact resistance versus ashing plasma (O$_2$ and H$_2$/N$_2$)

We used either O$_2$ or H$_2$/N$_2$ plasma in the ashing process carried out subsequent to etching process. When the amount of V_{dc} was high during the ashing process, the contact resistance increased significantly, as shown in Fig. 2(b). It should be noted, in particular, that even during an H$_2$/N$_2$ ashing process in which O$_2$ was not used, the contact resistance increased. We can easily determine that a thick oxidized layer is formed at the surface of CoSi$_x$ during an O$_2$ ashing process in which V_{dc} is very high. From this point on, therefore, we will focus on the case of H$_2$/N$_2$ in which the amount of V_{dc} is high.

IV. DISCUSSIONS

A. Surface analysis of CoSi$_x$ surface exposed to CH$_x$F$_y$ plasma

The thickness and the composition of the damaged layer were analyzed using XPS, SIMS, and TEM. Although we observed some difference in contact resistance between CF$_4$ and CH$_3$F, the SiO$_2$ concentration and the SiO$_2$ layer thickness at the CoSi$_x$ surface obtained by XPS and TEM were almost equal, as shown in Figs. 3(a) and 3(b). However, the SIMS result shows that the oxide concentration in the deep region of CoSi$_x$ is higher in the case where CH$_3$F is used than in the case where to CF$_4$ is used [Fig. 4(a)].

B. Analysis of ion penetration

Figure 5 shows the mass spectra of ions in the CH$_x$F$_y$ plasma measured by a quadrupole mass spectrometer (QMS).[10] The mass number of dominant ions (CH$_2$F$^+$; m/e =33) in CH$_3$F plasma was much lower than that (CF$_3^+$; m/e=69) in CF$_4$ plasma. Figure 6 shows the result of IEDF calculation of CH$_x$F$_y$ ions with V_{dc}=420 V. As can be seen from the figure, lighter ions were distributed over a wider energy range, i.e., had higher energy peaks. A MD simulation revealed that the dissociated C, H, and F species penetrate deeper in the case using CH$_2$F than using CF$_3$ (as shown in Fig. 7). This is because each ion has a different energy peak due to the mass number difference in the parent ions. To estimate the ion penetration depth, we used molecular dynamics simulation of Si–O–C–F–H system (because we have no MD potential set of Si–O–C–F–H–Co). Si was used as a substrate instead of CoSi$_x$. The depth of ion penetration can be estimated to be shallower because CoSi has higher film density. However, the ion mass dependence of penetration depth is considered to be similar. SIMS profile of O in Fig. 4

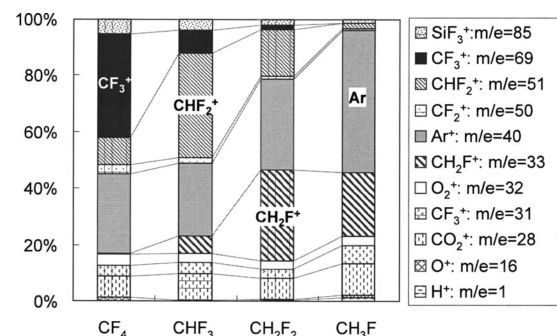

FIG. 5. Intensities of main mass numbers measured by QMS (SiO$_2$ film used for substrates).

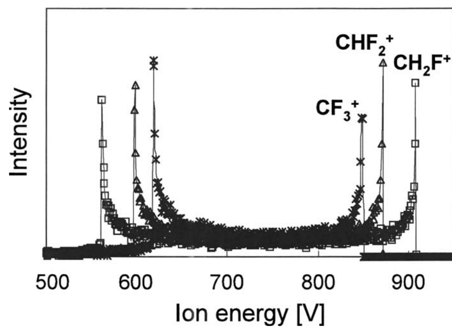

FIG. 6. Ion energy distribution function of $CH_xF_y^+$ ions at $V_{dc}=420$ V.

indicates that the CH_3F plasma affected the oxidation of Si substrate deeper than 50 nm. This value is much larger than the ion penetration depth estimated using MD and/or Monte Carlo simulations. However, actual CH_xF_y plasma generates not only CH_xF_y ions but also H ion and this small ion can penetrate deep into Si. Figure 8 shows the projection range (R_p) of ions as a function of incident energy using Monte Carlo simulation. The R_p of H^+ under 900 eV is about 12 nm and the maximum ion penetration depth is about four or five times deeper. Therefore, we estimated that "coinjection" of H ion promote the diffusion of O. Deeper damage caused by the ion penetration stimulates a deeper oxidation of $CoSi_x$ and increases the contact resistance.

C. Effect of ashing plasma on contact resistance

As mentioned before, the contact resistance increased even in H_2/N_2 ashing under a high V_{dc} content. The results obtained in XPS and TEM analyses revealed that oxidation of $CoSi_x$ surfaces increased in high V_{dc} content H_2/N_2 ashing [Figs. 3(c) and 3(d)]. Furthermore, depth profiles obtained by SIMS revealed an increase in oxidation in the deep region, as shown in Fig. 4(b). We believe that the increased resistance we observed is caused by this $CoSi_x$ oxidation.

The increase in contact resistance can be explained by the same mechanism in etching case. In this case, H ions penetrate much deeper than those of CH_xF_y because the mass number of H_3^+ ions ($m/e=3$) in H_2/N_2 plasma is much lower than that of $CH_xF_y^+$ ions. It is reported H ion induced the dislocation of Si atoms in the Si substrate and promote the oxidation during plasma treatment.[2] We estimated that H ion injection during H_2/N_2 ashing also induced the damage in $CoSi_x$ and Si. A deeply damaged $CoSi_x$ layer can easily be oxidized if it is exposed to air, resulting in increased resistance. This is proved by the result that the H profile obtained by SIMS analysis is similar to the O profile, as shown in Fig. 4(b). There was a significant positive correlation between the oxide concentration in the $CoSi_x$ under the SiO_2 layer formed at the surface and the contact resistance, as shown in Fig. 9. The schematic model of contact resistance increase is summarized in Fig. 10. To suppress the increase in contact resistance, it is essential to precisely control the ion energy as well as to properly select the ion species in the plasma process.

In situ processing before metallization (e.g., Ar sputtering or H_2 annealing) used in recent manufacturing lines is effective to remove thin oxidized layer. However, we suppose that

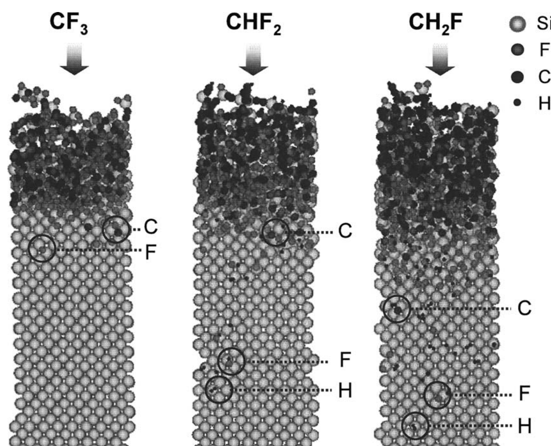

FIG. 7. $CH_xF_y^+$ ion penetration to Si substrate at $V_{dc}=200$ V calculated by MD.

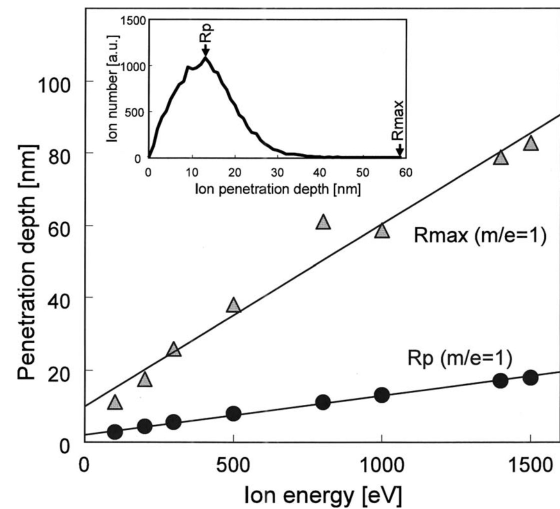

FIG. 8. Result of Monte Carlo simulation calculating the dependence of H^+ ($m/e=1$) ion penetration depth on ion energy. The maximum ion penetration depth (R_{max}) was four or five times deeper than the projection range (R_p).

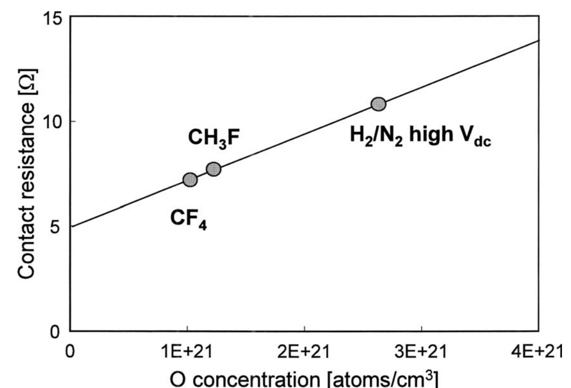

FIG. 9. Contact resistance as a function of the oxide concentration in $CoSi_x$.

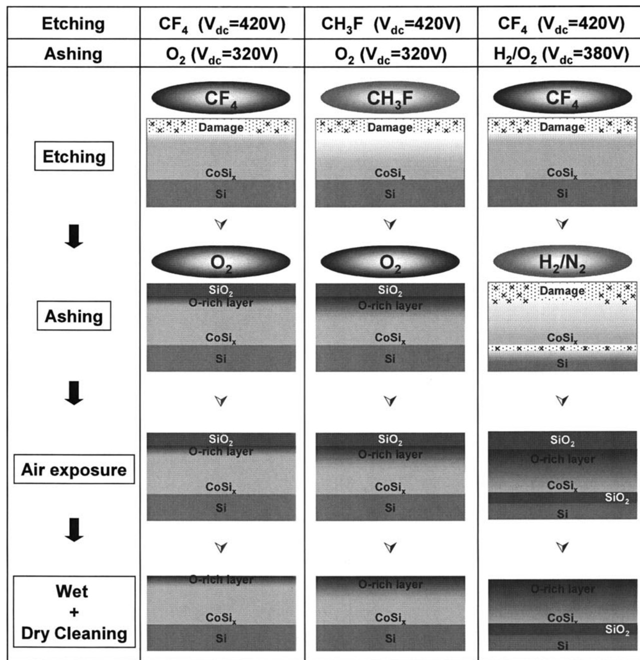

FIG. 10. Schematic model of contact resistance increase caused by plasma exposure.

it cannot remove such thick damaged layer. Furthermore, *in situ* processing might cause the faceting of via profiles and degrade the device performance. Therefore, the suppression of the damaged layer during via contact etching and ashing processes is indispensable to keep the low contact resistance, while the postetch treatment is also important as reported before.[7,8]

We suppose this result can be applied to the other silicides, e.g., NiSi or NiPtSi. The damaged Ni silicide can be also oxidized and causes the increase in the contact resistance. The ion penetration depth of $CoSi_x$ and $NiSi_x$ is thought to be similar since the typical film densities of $CoSi_2$ and $NiSi_2$ are 4.83 and 4.9 g/cm^3,[11] resulting in almost same oxidation thickness of both silicides.

V. CONCLUSION

We identified the mechanism of the contact resistance fluctuation caused by etching or ashing plasma processes. Plasma damage stimulates the oxidation of $CoSi_x$ during air exposure and results in increased contact resistance. When lighter ions are dominant in plasma, the contact resistance further increases. This is because lighter ions have a higher energy peak under the same V_{dc}, enabling them to penetrate deeper and cause more damage in $CoSi_x$. This was also demonstrated by MD simulation results we obtained. We observed that the contact resistance has a significant positive correlation with the oxide concentration in the $CoSi_x$. Thus, it can be concluded that it is essential to precisely control the ion energy as well as to properly select the ion species in the plasma process in the fabrication of next-generation semiconductor devices.

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