Silicon Wafer Gettering Design for Advanced CMOS Image Sensors Using Hydrocarbon Molecular Ion Implantation: A Review

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ABSTRACT We have developed silicon epitaxial wafers with high gettering capability using hydrocarbon molecular ion implantation for advanced Complementary Metal-Oxide-Semiconductor (CMOS) image sensors. These wafers have three unique silicon wafer characteristics for improvement of CMOS device electrical parameter such as high metallic impurity gettering, oxygen out-diffusion barrier effects from Czochralski silicon (CZ) substrate and hydrogen passivation effect for interface state defect at Si/SiO2. We demonstrate that double epitaxial growth silicon wafers have an extremely high gettering capability during CMOS device fabrication process. We also found that gettering capability strongly dependence on oxygen impurity amount in hydrocarbon molecular ion implantation projection range. We believe that this novel silicon wafer can drastically contribute to the improvement of CMOS image sensor device performance such as white spot defect and dark current.

INDEX TERMS CMOS image sensors, gettering, dark current spectroscopy, hydrocarbon molecular ion implantation, silicon wafers, white spot defect, atom probe tomography, electron spin resonance.

I. INTRODUCTION Complementary metal-oxide-semiconductor (CMOS) image sensors have widely been used in Internet of Thinking (IoT) devices such as smartphones, smart watch and personal computer tablets [1]. The consumer market strongly requires higher sensitivity and higher speed image data processing to realize high functional CMOS image sensors such as three dimensionally stacked back-side-illuminated CMOS image sensors (3D-CIS) [2]. However, there are some serious technological issues in the fabrication of advanced CMOS image sensors as shown in Fig. 1.

The first important issue is the metallic impurity contamination of the pixel active region during 3D-CIS fabrication [3]. In the case of the front end of line (FEOL) process for 3D-CIS fabrication, gettering sinks in a silicon wafer bulk are eliminated by backside grinding and chemical mechanical polishing (CMP). Only, the epitaxial silicon layer remains after the FEOL process. The pixel die is bonded to the image signal processor (digital signal processor) die using Cu-Cu through silicon via (TSV) and surface activated bonding at low temperature (hybrid bonding process) [4]. Cu can very easily diffuse to a silicon crystal bulk from Cu-Cu TSV during low temperature annealing [5]. Copper metallic impurities form deep energy levels in the pixel active region. These defects affect electrical device performance such as photodiode junction leakage current, white spot defect and dark current. Thus, in CMOS image sensor manufacture much effort has been made to eliminate metallic impurities from the pixel active region using the gettering technique.

The intrinsic gettering (IG) technique has been commonly used in semiconductor manufacturing since 1980 [6], [7].
IG can getter metallic impurities through oxygen precipitation growth in the silicon crystal bulk during CMOS device heat treatment. Oxygen precipitates act as gettering sinks for metallic impurities. However, the thermal budget of CMOS device heat treatment and the process duration tend to decrease year by year. Thus, oxygen does not precipitate sufficiently to grow and become effective gettering sinks under low thermal budget condition. Moreover, the gettering sinks in the silicon wafer bulk (oxygen precipitate region) eliminated by backside grinding and CMP after the FEOL process. IG is not a beneficial technique for 3D-CIS fabrication.

Consequently, Kuroi et al., proposed that proximity gettering sinks formed under device active regions using a mega-electron-volt high energy ion implantation technique in the CMOS device fabrication process [8]. However, this technique induces ion implantation damage. In case of low temperature CMOS device fabrication processes, it is extremely difficult to repair this implantation damage in a CZ silicon substrate. These defects degrade the yield and performance of electron devices.

The other technical solution is the implantation of high (\(>1\times10^{16}\) cm\(^{-2}\)) dose of helium (He) and hydrogen (H) ions into the top surface of CZ silicon substrate [9], [10]. These He and H ion implantations form microscopic cavities in bulk crystalline silicon. The cavities form effective gettering sinks that can getter metallic impurities in bulk crystalline silicon. However, the process fabrication cost is generally higher than that of the conventional ion implantation process, because forming the cavities requires very high ion implantation doses and very long implantation process time. Thus, it is very difficult for silicon wafer manufacturers to produce He and H-implanted silicon wafers in mass silicon wafer manufacturing processes.

The second important issue is oxygen out-diffusing to the pixel active region from the czochralski silicon (CZ) substrate during CMOS device heat treatment. The CZ-silicon substrate contains oxygen impurities in the bulk during the crystal growth. Oxygen out-diffuses formed oxygen related deep energy level defects in the silicon bandgap. These defect strongly affect electrical device performance such as perfect charge transfer operation. Alternative CZ-silicon substrates have low oxygen contents for crystal growth in CMOS image sensor fabrication. A low oxygen content in the CZ-silicon substrate decreases the amount of oxygen out-diffusing during the CMOS image sensor fabrication. However, a low oxygen containing CZ-silicon substrate can not provide sufficient mechanical strength under the device thermal budget. Such a substrate will have enhanced of dislocation and dislocation loops in the device active region during device heat treatment. Thus, it is not effective resolving the second issue.

The third important issue is the question of white spot defects and dark current induced by interface state defects (DIT) between at the bonding interface pixel die and the image sensor processing die, the shallow trench isolation (STI) region and the deep trench isolation (DTI) region. DIT act as generation-recombination centers (G-R). Thus, DIT in CMOS device manufacture have been controlled by low temperature hydrogen forming gas annealing (FGA). Hydrogen in-diffuses to the pixel active region from hydrogen gas atmosphere. FGA can passivate DIT to form non-electrical active defects by through hydrogen termination. However, in a typical 3D-CIS fabrication process, multi-dielectric films are often used with metallic wire deposition which in the pixel region. Hydrogen cannot diffuse to the pixel region. We call the hydrogen diffusion barrier effects. It is very difficult to use FGA in 3D-CIS fabrication.

Therefore, we have seriously considered resolutions to these technological issues in 3D-CIS fabrication. We have developed a new epitaxial silicon wafer with gettering capability for 3D-CIS fabrication using the hydrocarbon molecular ion implantation technique in 2011 [11].

We found that this novel silicon wafer has three unique silicon wafer characteristics. The first is, its very high gettering capability for metallic impurities in the pixel active region during CMOS image sensor fabrication process [12], [13]. The second is, its oxygen out-diffusion barrier effect, which presents oxygen from out-diffusing to the device active region from the CZ silicon substrate during device heat treatment [14]. The third is, its hydrogen passivation effect on interface state defects at the Si/SiO\(_2\) interface [15]–[17].

In this review article, we demonstrate that the unique characteristics of this novel silicon wafers has high gettering capability and the passivation effect on interface state defects in CMOS image sensor fabrication. Moreover, we determine the effects of white spot defect and dark current on the CMOS image sensors fabricated with and without hydrocarbon molecular ion implantation.

We demonstrate that the novel silicon wafer has markedly decreases the white spot defects as evaluated by dark current spectroscopy. It is extremely important to understand the production properties of the hydrocarbon molecular ion implanted epitaxial silicon wafer for industrial application such as 3D-CIS. We propose a solution to 3D-CIS fabrication issues by designing a silicon wafer gettering technique using hydrocarbon-molecular-ion-implantation to
achieve a high-functional performance of advanced CMOS image sensors.

II. CONCEPT OF PRODUCTION OF HYDROCARBON-MOLECULAR-ION IMPLANTED EPITAXIAL SILICON WAFERS

Figure 2 shows the concept of production of hydrocarbon-molecular-ion-implanted epitaxial silicon wafers [9]. First, molecular ion implanted silicon wafer top surface without oxidation film and additional recrystallization heat treatment. Implanted molecular ion formed carbon and hydrogen ion projection range after ion implantation. Second, the epitaxial layer is formed on the hydrocarbon-molecular-ion-implanted silicon wafer surface by chemical vapor deposition. Thus, the production concept for this novel silicon wafer is extremely simple.

Figure 3 shows the secondary ion mass spectroscopy (SIMS) depth profile measured on hydrocarbon-molecular-ion-implanted epitaxial silicon wafers after epitaxial growth [9]. The hydrocarbon molecular ion projection range consists of carbon and hydrogen implantation elements. In this projection range, the carbon peak concentration is $8 \times 10^{19}$ cm$^{-3}$, the hydrogen peak concentration is $1.2 \times 10^{18}$ cm$^{-3}$ and the oxygen peak concentration is $6 \times 10^{18}$ cm$^{-3}$. The carbon peak concentration is three orders of magnitude higher than the solid solubility of carbon impurities in the silicon crystal. The oxygen concentration in top epitaxial layer is $2 \times 10^{16}$ cm$^{-3}$ without hydrocarbon molecular ion implantation after epitaxial growth.

III. CHARACTERISTIC OF HYDROCARBON MOLECULAR ION IMPLANTED EPITAXIAL SILICON WAFER

A. GETTERING CAPABILITY OF HYDROCARBON MOLECULAR ION IMPLANTED EPITAXIAL SILICON WAFERS

Figure 4 shows the copper (Cu) and nickel (Ni) metallic impurities gettered in the hydrocarbon molecular ion projection range after surface metallic contamination and diffused heat treatment. The initial Cu and Ni surface metallic impurity concentration at a level of $1 \times 10^{13}$ atoms/cm$^2$ on their surfaces [9]. This figure indicates that the metallic impurities diffused to the hydrocarbon ion projection range during heat treatment. Thus, the metallic impurities were gettered in the hydrocarbon molecular ion projection range after heat treatment. Thus, this novel silicon wafer has high gettering capability for metallic impurities after heat treatment.

B. HYDROGEN PASSIVATION EFFECT OF HYDROCARBON-MOLECULAR-ION IMPLANTED EPITAXIAL SILICON WAFERS

Figure 5 shows the interface defect (DIT) density at the Si/SiO$_2$ interface of metal oxide semiconductors (MOS) fabricated with and without hydrocarbon-molecular-ion implanted epitaxial silicon wafers after annealing at (a) 500°C and (b) 700°C [14]. DIT density was analyzed by capacitance-voltage measurement (C-V) using
FIGURE 5. Dit density of wafers after annealing at (a) 500 °C and (b) 700 °C without (blue squares) and with (red diamonds) hydrocarbon ion implantation and before annealing without (black circles) hydrocarbon ion implantation. Reproduced with permission. Copyright (2020) The Japan Society of Applied Physics.

FIGURE 6. Dit density at midgap of wafers after annealing at 500 °C, 600 °C, 700 °C, 800 °C and 900 °C without and with hydrocarbon ion implantation. Reproduced with permission. Copyright (2020) The Japan Society of Applied Physics.

MOS. It is well known that DIT origin is Si/SiO₂ interface structure defect such as Pb₀ center. A Pb₀ center has a structure of one silicon atom bonded to three silicon atoms at the interface and is designated as Si≡Si₃ [18]. Pb₀ centers form deep energy level defects in the bandgap of SiO₂. These deep energy level defects act as G-R centers. Density of Pb₀ centers is determined by electron spin resonance (ESR) spectroscopy [19].

The mid-gap level (0.5eV) in DIT density of silicon wafer without C₃H₅ implantation at 500°C is lower than that of silicon wafer without C₃H₅ implantation at 700°C as shown in Figs. 5 and 6. The DIT density of silicon wafer without C₃H₅ implantation decreased at 500°C may be a passivation effect of thermal strain induced by thermal stress in nitrogen ambient.

The DIT density of silicon wafers without C₃H₅ implantation at 700°C increased with the annealing temperature which can be explained by two possibilities. One is DIT generation due to Si-O bond breaking induced by compressive stress generated during annealing. The other is the dissociation of hydrogen at the Si/SiO₂ interface during anneal treatment.

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Figure 7 shows the DIT density at the Si/SiO₂ interface versus density of Pb₀ centers at each annealing temperature in wafers without and with hydrocarbon ion implantation. Reproduced with permission. Copyright (2020) The Japan Society of Applied Physics.

FIGURE 7. Dit density at Si/SiO₂ interface versus density of Pb₀ centers at each annealing temperature in wafers without and with hydrocarbon ion implantation. Reproduced with permission. Copyright (2020) The Japan Society of Applied Physics.

C. RESULTS OF WHITE SPOT AND DARK CURRENT EVALUATION OF HYDROCARBON-MOLECULAR-ION-IMPLANTED EPITAXIAL SILICON WAFERS BY DARK CURRENT SPECTROSCOPY

Figure 8 shows the cross-sectional schematic of silicon wafers used for the evaluation of white spot defects and dark current by dark current spectroscopy (DCS) [20]. Onaka-Masada et al. fabricated four transistor type pinned photodiode CMOS image sensors using the CMOS device fabrication process for DCS measurement. DCS is an extremely powerful tool for metallic impurity contamination analysis in charge-coupled devices (CCD) and CMOS image sensors [20]. The experimental parameters were epitaxial growth layer thickness (single and double deposited epitaxial layers) and hydrocarbon molecular ion implantation position in silicon the wafers without hydrocarbon implantation is proportional to the density of Pb₀ centers. Moreover, the DIT density of the hydrocarbon-implanted silicon wafer with anneal at 700°C drastically decreased compared to other silicon wafers. Okuyama et al., assume that diffused hydrogen terminated silicon dangling bond such as Pb₀ centers by Si-H bonding formation at the Si/SiO₂ interface [17]. Therefore, hydrocarbon-molecular-ion implanted silicon wafers have the passivation effect through hydrogen termination, which decreases the DIT density at the Si/SiO₂ interface with structural defects such as Pb₀ centers.
Figures 9 and 10 show the measurement results of white spot defect counts and dark current using both fabricated CMOS image sensors and DCS [21]. The white spot defect counts and dark current of wafers with hydrocarbon molecular ion implantation are lower than those without it. It is well known that there are three components of the dark current at photodiode junction ($I_{\text{dark}}$) in CMOS image sensor pixels. $I_{\text{dark}}$ is forming the diffusion current ($I_{\text{diff}}$), generation current ($I_{\text{gen}}$) and surface generation ($I_{\text{sur}}$). The first two components are related to the process induced defects such as metallic impurity related deep level defects, and the last is related to the Si/SiO$_2$ interface at transfer gate transistor in CMOS image sensor pixels. Okuyama et al., reported that hydrogen diffused to the MOS device active regions from hydrocarbon molecular ion implantation projection range during MOS device fabrication process which can reduce interface state density at the Si/SiO$_2$ interface such as P$_b$ centers [17].

Hydrogen diffusion amounts of single and double epitaxial growth silicon wafers from hydrocarbon implantation projection range are 8.1x10$^{12}$ and 8.5x10$^{12}$ cm$^{-2}$, respectively, calculated by SIMS analysis before and after device process. It is not significant difference hydrogen diffusion amount during CMOS device process. Thus, hydrocarbon ion implanted single and double epitaxial growth silicon wafer have higher reduction capability of surface generation ($I_{\text{sur}}$) component in the dark current compare than that of dark current without implantation.

Moreover, the white spot defect counts of double epitaxial silicon wafer is 40% lower compare than that of without implantation. This result indicates that the hydrocarbon molecular-ion-implanted double epitaxial growth silicon wafers have higher gettering capability than the other silicon wafers.

Onaka-Masada et al., have determined the reason for the above results by atom probe tomography (APT) [20]. APT is a very useful tool for atomic-level impurity distribution analysis in semiconductor materials. Onaka-Masada et al., found that the hydrocarbon molecular ion implantation generates hydrocarbon-ion –related-defects such as carbon-related defects (C-I) in implantation projection range after CMOS device fabrication [20].

Figure 10 shows the carbon and oxygen impurity distributions in hydrocarbon-molecular-ion-related defects of the single and double epitaxial growth silicon wafers after CMOS device fabrication process analyzed by APT. Initial oxygen concentration in epitaxial layer is much lower (<1x10$^{16}$cm$^{-3}$) than that in CZ silicon substrate (<1x10$^{19}$cm$^{-3}$) before device fabrication process [20]. And oxygen diffusion length of single epitaxial growth silicon wafer from CZ silicon substrate is shorter than that of double epitaxial growth silicon wafer. As a results, oxygen diffusion amount of single epitaxial growth silicon wafer is higher than that of double epitaxial growth silicon wafer during CMOS device heat process. Therefore, single epitaxial growth silicon wafer in implantation projection range forms oxygen containing carbon-related defects (we call them C-I-O). And double epitaxial growth silicon wafer does not form C-I-O. Double epitaxial growth silicon wafer form carbon-related defects (C-I). This result indicates that C-I can act as effective gettering sinks for metallic impurities in the hydrocarbon molecular ion implantation projection range. Figure 11 shows the physical model of the gettering reaction of hydrocarbon molecular ion implanted silicon wafers. In the case of double epitaxial growth silicon wafers, C-I strongly interacts with metallic impurities in the hydrocarbon molecular ion projection range [20], [22]. The C-I has high binding energy with metallic impurities determined by density functional first principles calculation [23], [24]. In contrast, in the case of a single epitaxial silicon wafer, C-I-O does not strongly interacts with metallic impurities in the hydrocarbon molecular ion implantation projection range. The gettering capability strongly depends on the amount of oxygen as shown in Fig. 10. The very important key factor for improving the metallic impurity gettering capability of hydrocarbon-implanted-epitaxial silicon wafers is the amount of oxygen in gettering sinks during CMOS image sensor fabrication.
IV. SILICON WAFER DESIGN FOR 3D-CIS

A. WHAT IS THE BEST SILICON WAFER GETTERING DESIGN FOR 3D-CIS?

3D-CIS have been manufactured for the consumer smartphone market, because their quantum efficiencies and image data processing are higher than those of conventional front-illuminated CMOS image sensors. However, there are serious technical issues in the 3D-CIS fabrication. The very important issue is the copper metallic impurity contamination of the pixel active region during TSV fabrication.

Another issue is the formation of interface state defects at the interface between the pixel die and the image sensor processor after bonding. Thus, we propose that the technical issues solution using hydrocarbon-molecular-ion implanted double epitaxial growth silicon wafers. There are two reasons as follow.

Conventional back-side-illuminated (BSI) CMOS image sensors fabricated by using single epitaxial growth silicon wafers without gettering sinks (conventional epitaxial silicon wafers such as p/p+). In BSI fabrication, only the epitaxial growth layer remains after FEOL and there is no gettering layer in the epitaxial layer.

In contrast, the hydrocarbon-molecular-ion-implanted double epitaxial silicon wafers have gettering sinks in the epitaxial layer as shown in Fig. 8. These wafers have gettering sinks remaining in the epitaxial layer after FEOL. Thus, they have high gettering capability for metallic impurities during CMOS device fabrication as shown in Fig. 9.

Second, hydrocarbon-molecular-ion-implanted epitaxial growth silicon wafers have the hydrogen passivation effect which decreases DIT density at the Si/SiO₂ interface after annealing as shown in Fig. 7. These double epitaxial growth silicon wafers can decreases DIT density at the bonded die interface, STI and DTI regions. However, conventional epitaxial silicon wafers do not have the hydrogen passivation effect in the epitaxial layer.

Therefore, we strongly recommend the use of hydrocarbon-molecular-ion-implanted double epitaxial growth silicon wafers for 3D-CIS fabrication.

V. CONCLUSION

The fabrication of advanced CMOS image sensors has some serious technical issues. The very important issue is the metallic impurity contamination of the pixel active region of CMOS image sensors during 3D-CIS fabrication. Thus, we developed a gettering silicon wafer using a hydrocarbon molecular ion implantation technique.

We demonstrated that double epitaxial growth silicon wafers have a very high gettering capability during CMOS image sensor fabrication. We found that the gettering capability strongly depends on the amount of oxygen impurities in the hydrocarbon molecular ion implantation projection range. Moreover, these novel silicon wafers can markedly decrease the DIT density at the Si/SiO₂ interface through the termination of silicon dangling bonds such as those in Pb₀ centers.

We also found that these wafers can decrease the white spot defect density and dark current in CMOS image sensor manufacturing. Therefore, we believe that these novel silicon wafers can contribute to the improvement of the performance of advanced CMOS image sensor.

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