Material characterization for advanced Si LSI process technology by means of positron annihilation

A Uedono¹, N Oshima², T Ohdaira³, R Suzuki² and S Ishibashi³

¹ Division of Applied Physics, Faculty of Pure and Applied Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
² Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan
³ Nanosystem Research Institute (NRI) “RICS”, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan

E-mail: uedono.akira.gb@u.tsukuba.ac.jp

Abstract. Vacancy-type defects in gas cluster ion implanted Si and electroless deposited Cu were studied by monoenergetic positron beams. For Ar gas cluster ion implanted Si, we found that the vacancy-rich region was localized at a depth of 0-13 nm. Two different defect species were found to coexist in the damaged region, and they were identified as divacancy-type defects and vacancy clusters filled with Ar. For electroless deposited Cu films, the major defect species were identified as vacancy complexes ($V_3-V_4$) and larger vacancy clusters (~$V_{10}$). Annealing behaviours of the defects and the relation between the defects and impurities were also discussed. We have demonstrated the efficacy of positron annihilation to aid in the optimization of process parameters for advanced Si LSI processes.

1. Introduction

Developments of Si-technology based industries and the qualities of their products mainly depend on the ability to decrease the size of integrated circuits [1]. The first transistor was made by eyes and fingers in 1947, but a third dimension 22-nm high-$k$/metal gate transistor was now shown to be a production level. Modern semiconductor devices are fabricated though numerous processing steps. They are separated into two major categories; front-end-of-line (FEOL) and back-end-of-line (BEOL). FEOL processing refers to the formation process of transistors such as junction formation, insulator/metal-gate fabrication, etc. BEOL refers to the process connects those transistors using metal wires isolated by dielectric layers. Significant efforts to introduce new materials have been made in order to achieve “scaling”. However, one often faces the difficulties in the control of materials properties which caused by atomic scale disorders. We have shown that the positron annihilation technique is a powerful characterization tool for modern Si-technology related materials, and can contribute developments of both FEOL and BEOL processing [2-10]. In the present paper, as typical applications of this technique to those processing technologies, we report studies of defects in ultra-shallow region of gas cluster ion implanted Si and in electroless deposited Cu for composite barrier/seed layers of Cu interconnects.

The gas cluster ion beam (GCIB) is based on electrostatic acceleration of charged cluster ions with a few hundred to thousands of atoms or molecules. This technique and related phenomena have been extensively studied because of its unique characteristics [11]. It has been suggested that GCIBs have
great potential as a tool for ultra-shallow implantation, high yield sputtering, surface smoothing, ion-assisted deposition/modification, and time-of-flight secondary ion mass spectrometry. When cluster ions are implanted into solids, high density electric excitation states of the targets and the projectile are created. The defect-introduction mechanism and resultant damage by GCIBs are therefore thought to differ from those for conventional ion implantation. Cu interconnects and related technologies have been extensively developed to meet requirements of high-performance metal lines used in modern ULSI devices. The dual damascene scheme using electroplated Cu is the mainstream technology [1]. Recently, composite barrier/seed layers using physical vapor deposition and electroless Cu plating are proposed to obtain an efficient bottom-up fill during Cu electroplating [12]. The integration of an electroless Cu process into the Cu metallization process, however, requires detailed knowledge about the behavior of Cu atoms and impurities which may affect blistering and post-anneal void formation.

2. Experiments
The samples investigated were Ar and B cluster ion implanted Si fabricated using a GCIB developed by TEL Epion Inc. [13]. Neutral clusters were generated by adiabatic expansion of Ar and B2H6/He gas into a vacuum chamber, and they were ionized by electron bombardment. Ionized clusters with a mean size of 2×10^5 atoms were implanted with energy of 20 - 60 keV to Cz-Si. The cluster ion doses were 1×10^14 cm^-2 and 2.5×10^13 cm^-2 for Ar and B gas clusters, respectively.

ELD-Cu films with high and low residual impurity concentrations were deposited with a novel electrolyte using a metal ion complex as a reducing agent [14] to eliminate hydrogen evolution during the electroless plating process (hereafter, these are referred as ELD-Cu(H) and ELD-Cu(L)). The thickness of ELD-Cu(H) and ELD-Cu(L) were 1.6 and 2.3 μm, respectively. For ELD-Cu(H), the major impurity species are nitrogen (10^21 cm^-3), carbon (10^20 cm^-3), oxygen (10^19 cm^-3), and sulfur (10^19 cm^-3). For ELD-Cu(L), these concentrations are an order of magnitude lower. The mean grain size is calculated to be 150 and 540 nm for ELD-Cu(H) and ELD-Cu(L), respectively. Isochronal annealing is performed up to 750°C in vacuum (60 min).

With a monoenergetic positron beam, the Doppler broadening spectra of the annihilation radiation were measured with a Ge detector as a function of the incident positron energy E. The low-momentum part was characterized by the S parameter, defined as the number of annihilation events over the energy range of ±1 keV in the energy range of ±1 keV (where ΔEγ=0.76 keV) around the center of the peak. The relationship between S and E was analyzed to obtain the depth distribution of S [15]. We also used a coincidence-detection system, and the obtained spectra were compared with those theoretically calculated using QMAS (Quantum MATERials Simulator) code based on the projector augmented-wave (PAW) method [16]. The (S,W) value was used to identify the defects, where the W value calculated from the tail of the Doppler broadening spectrum in the range of 3.4 keV≤|ΔEγ|≤6.8 keV. The lifetime spectra of positrons were also measured using a pulsed monoenergetic positron beam, and analyzed using RESOLUTION computer program [17].

3. Results and discussion

3.1. Vacancy-type defects in gas cluster ion implanted Si
Figure 1 shows the S values of Ar and B gas cluster implanted Si as a function of incident positron energy E. For Ar gas cluster implanted samples, the S value at low E (1 keV) was larger than the S value for defect-free Si (at E≥20 keV), suggesting the annihilation of positrons trapped by vacancy-type defects introduced by the implantation. The solid curves are fits to the experimental data, and the derived depth distributions of the S values are shown in Fig. 2. For all samples, the damage depth was 10-13 nm. The projected range of monomer Ar^+ with energy of 10 keV is about 15 nm, which is close to the damaged area shown in Fig. 2. In the present experiment, however, the average energy of each monomer ion is an order of 10 eV. A cluster ion interacts with the surface almost simultaneously, and deposits its energy into a very small volume of the target material. The impact area of gas cluster ion implantation thus experiences extremely high temperature and pressure/temperature transients, which
cause non-linear implantation effects. The observed extremely deep damaged region can be attributed to such properties of cluster ion implantation.

Lifetime spectra of positrons for Ar gas cluster implanted Si were measured at \( E=1 \) keV. The measured spectra were decomposed into two components, the short- and long-lived positron lifetimes, \( \tau_1 \) and \( \tau_2 \), and the intensities for the long-lived component, \( I_2 \), are shown in Fig. 3. No large change in the lifetimes was observed for the samples with different Ar gas cluster acceleration energies. The value of \( \tau_1 \) is close to the lifetime of positrons trapped by a divacancy \( V_2 \), which is typical for vacancy-type defects introduced by conventional ion implantation. In the present experiments, because the damaged region was expected to be amorphous [11], the defects detected by the first component are considered to be the open spaces which have an open space close to that of \( V_2 \). The defects detected by the second component can be identified as large vacancy-clusters, where the open space of such defects could be larger than that of \( V_{10} \) [18]. The value of \( I_2 \) increased with increasing gas cluster acceleration energy, suggesting an increase in the concentration of the vacancy clusters, and this was an origin of the increase in the \( S \) value observed for those samples.

Figure 4 shows the \( S-W \) relationships for gas cluster ion implanted samples measured using the

**Figure 1.** \( S \) parameters as a function of incident positron energy \( E \) for gas cluster ion implanted Si. The solid curves are fits to the experimental data.

**Figure 2.** Derived depth distributions of \( S \) from the \( S-E \) curves shown in Fig. 1.

**Figure 3.** Lifetime of positrons (\( \tau_1 \) and \( \tau_2 \)) and the second intensity (\( I_2 \)) for gas cluster ion implanted Si.

**Figure 4.** \( S-W \) relationships for gas cluster ion implanted Si, and the \((S,W)\) values calculated by the PAW method. The \((S,W)\) values for the damaged region for plasma immersion B-implanted Si before and after spike RTA were also shown [5].
coincidence-detection system at $E=1$ keV. The $(S,W)$ values obtained using the PAW method are also shown, where calculations were made for the annihilation of positrons in the delocalized state (DF: defect free) and typical vacancies such as $V_2$-$V_{10}$. The obtained $S$ and $W$ values for Ar gas cluster implanted Si were smaller (or larger) than those for $V_2$. This means that the momentum distribution of electrons in the vacancy-type defects introduced by Ar gas cluster implantation was modified from that of 'pure' vacancies. Maekawa and Kawasuso [18] studied high-dose He-implanted Si using positron annihilation and the first-principles calculation. They reported that the trapping of positrons by He-storing microvoids enhanced the annihilation rate of high-momentum electrons. In the present experiment, therefore, a candidate for the modification is the trapping of positrons by Ar-storing vacancy-clusters (micro gas bubbles). In general, inert gas storing defects are clearly observed after post-implantation annealing. Simpson et al. [19] reported that the annealing temperature ramp-rate had a significant impact on residual defects for He-implanted Si. They found that the $S$ value increased with an increasing ramp-rate, suggesting that the formation of He-related defects was accelerated by increasing the ramp-rate. In the present experiment, Ar-storing clusters (the second component: $\tau_3=514$ ps) were observed without annealing. Thus, the formation of micro gas bubbles can be attributed to the extremely high temperature and its rapid gradient in impact regions of Ar gas clusters.

As shown in Figs. 1 and 2, for B gas cluster implanted Si, the $S$ value in the damaged region was smaller than that for defect free Si. In Fig. 3, the lifetime of positrons (360±1 ps) for this sample was longer than the defect-free lifetime. In Fig. 4, the $(S,W)$ values for the damaged region for plasma immersion B-implanted Si before and after spike rapid thermal annealing (RTA, 1075°C) were shown [5]. For the as-implanted sample, the $(S,W)$ value was close to the calculated value for $V_1$B$_2$ (four Si atoms were removed and two B atoms were inserted into substitutional sites), suggesting that major defect species is such a vacancy-boron complex. After RTA, the $S$ ($W$) value was smaller (larger) than the value for defect-free Si, and the relationship between the $(S,W)$ values for defect-free Si and the damaged region was close to that for calculated defect-free Si and an icosahedral B cluster [20] ($V_2$B$_{12}$), where the damaged region was crystal after RTA and the calculation of $V_2$B$_{12}$ was done for the crystalline structure. For B gas cluster ion implanted Si, the observed $(S,W)$ value was apart from the calculated value for $V_2$B$_{12}$, but lie along the line connecting the values for defect-free Si and for the plasma immersion B-implanted Si after RTA. The difference between the $(S,W)$ value for B gas cluster and plasma immersion B-implantations could be due to an amorphousization of Si matrix by gas cluster implantation, and a resultant enhancement of the effect of B clusters on the $(S,W)$ value.

3.2. Agglomeration and dissociation of vacancies in ELD-Cu

Figure 5 shows the $S$–$E$ curves for ELD-Cu(H) before and after annealing. Since the $S$ value for the defect-free Cu was measured to be 0.4160 [10], the observed large $S$ value for ELD-Cu is due to the annihilation of positrons trapped by vacancy-type defects. The depth distributions of $S$ were obtained from the $S–E$ curves and the results are shown in Fig. 6. For the as-deposited sample, the $S$ value starts to increase at <800 nm. Thus, the vacancy-type defects introduced after the deposition diffuse toward the surface and agglomerate in the subsurface region. After annealing at 170°C, the $S$ value at $E=2$ keV increases. This corresponds to defect agglomeration in the region of <50 nm. As shown in Fig. 6, SIMS measurements show that the sulphur concentration increases near the surface for the sample annealed at 170°C. Vacancies and sulphur both tend to migrate to the surface. Their interaction and the resultant formation of vacancy-impurity complexes determine the annealing behavior of vacancy-type defects. For the sample annealed above 300°C, such vacancy agglomerates are annealed out. At 740°C, the $S$ value below 1200 nm is higher than that in the shallower region, suggesting that vacancy-type defects exist near the Cu/barrier-metal interface even at this temperature and that the Cu/barrier-metal interface does not act as a sink for vacancies.

Figure 7 shows $S$ at $E=18$ keV for ELD-Cu(H), ELD-Cu(L) and electroplated Cu with high and low residual impurity concentrations [E-Cu(H) and E-Cu(L)] [21]. For ELD-Cu(L) before annealing, the $S$ value is smaller than that for ELD-Cu(H), suggesting that the mean size (and/or concentration) of vacancy-type defects increases with increasing residual impurity concentration. This is attributed to an
interaction between vacancies and impurities, and the resultant formation of vacancy-impurity complexes. For ELD-Cu(L) and E-Cu(H), the observed increase of $S$ in the temperature range between 200-400°C corresponds to the agglomeration of vacancy-type defects, which is close to the annealing stage of vacancy-type defects in light-particle irradiated Cu (stage V) [22]. Since the residual impurity concentration in ELD-Cu is higher than that in E-Cu, the annealing of defects requires higher temperature for Cu films with high impurity concentration.

Figure 8 shows the results of positron lifetime measurements on ELD-Cu(H) as a function of annealing temperature. It was found that $\tau_2$ to be almost constant (350 ps), but $\tau_1$ decreases from 250 ps to 120 ps with increasing annealing temperature. Using these results, the defect species detected by the first and second component can be identified as vacancy complexes ($V_2$-$V_4$) and larger vacancy clusters (such as $V_{10}$, ref. 23), respectively. The intensity corresponding to the vacancy clusters ($I_2$) decreases after 750°C annealing, corresponding to the decrease in $S$ in this temperature range. Although the size of vacancy clusters is stable in the temperature range below 750°C annealing, that of the vacancy complexes ($V_2$-$V_4$) decreases with increasing temperature. Because the ‘pure’ vacancies with the size of $V_2$-$V_4$ are unstable at 600-800°C, they must couple with residual impurity to make stable complexes.
4. Conclusions
We have demonstrated the efficacy of positron annihilation for the characterization of vacancies in ultra-shallow region in Si and electroless deposited Cu to aid in the optimization of process parameters for those materials. For gas cluster ion implanted Si, we found that the formation of the vacancy clusters was affected by extremely high temperature and its rapid transients in the impact regions of gas cluster ions. For ELD-Cu, the close relationship between annealing behaviours of vacancy-type defects and residual impurities was observed, suggesting that the precise control of impurities in Cu is a key to suppress the atomic migration and to increase the reliability of Cu interconnects.

References
[1] International Technology Roadmap for Semiconductors 2011, www.itrs.net.
[2] Uedono A, Inoue N, Hayashi Y, Eguchi K, Nakamura T, Hirose Y, Yoshimaru M, Oshima N, Ohdaira T and Suzuki R 2009 Jpn. J. Appl. Phys. 48 120222
[3] Uedono A, Inoue N, Hayashi Y, Eguchi K, Nakamura T, Yoshimaru M, Oshima N, Ohdaira T and Suzuki R 2009 Proc. 12th IEEE Int. Interconnect Tech. 75
[4] Uedono A, Inoue N, Hayashi Y, Eguchi K, Nakamura T, Hirose Y, Yoshimaru M, Oshima N, Ohdaira T and R. Suzuki 2010 Proc. 13th IEEE Int. Interconnect Tech. Conf. 7.2
[5] Uedono A, Tsutsui K, Ishibashi S, Watanabe H, Kubota S, Nakagawa Y, Mizuno B, Hattori T and Iwai H 2010 Jpn. J. Appl. Phys. 49 051301
[6] Uedono A, Tsutsui K, Ishibashi S, Watanabe H, Kubota S, Tenjinbayashi K, Nakagawa Y, Mizuno B, Hattori T and Iwai H 2010 Proc. 10th Int. Workshop on Junction Technology 149
[7] Oka Y, Uedono A, Goto K, Hirose Y, Matsuura M, Fujisawa M and Asai K 2011 Jpn. J. Appl. Phys. 50 05EB06
[8] Uedono A, Moriya T, Tsutsui T, Kimura S, Oshima N, Suzuki R, Ishibashi S, Matsui H, Narushima M, Ishikawa Y, Graf M and Yamashita K 2010 12th Int. Workshop on Junction Technology Extended Abstracts IEEE Press 85
[9] Uedono A, Dordi Y, Li S, Mizunaga G, Tenjinbayashi K, Oshima N and Suzuki R 2012 IEEE Int. Interconnect Tech. Conf. Session 9.4
[10] Uedono A, Yamashita Y, Tsutsui T, Dordi Y, Li S, Oshima N and Suzuki R 2012 J. Appl. Phys. 111 104506
[11] Yamada I, Matsuo J, Toyoda N and Kirkpatrick A 2001 Mat. Sci. Eng. R 34 231
[12] Webb E, Witt C, Andryuschenko T and Reid J 2004 J. Appl. Electrochem. 34 291
[13] Bachand J, Freytsis A, Harrington E, Gwinn M, Hofmeester N, Hautala J, Mack M E and Regan K 2002 Proc. Ion Implantation Technology IEEE, New York 669
[14] Vaskelis A, Norkus H J, Rozovskis G and Vinkevicius H I 1997 Trans. IMF 75 1
[15] Van Veen A, Schut H, De Vries J, Hakvoort R A and Ijpma M R 1990 AIP Conf. Proc. 218 171
[16] Detailed and up-to-date information of QMAS is reported in http/qmas.jp
[17] Kirkegaard P, Eldrup M, Mogensen O E and Pedersen N J 1981 Comput. Phys. Commun. 23 307
[18] Maekawa M and Kawasuso A 2010 J. Phys.: Conf. Ser. 225 012032
[19] Simpson P J, Knights A P, Chicoine M, Dudeck K, Moutanabbir O, Ruffell S, Schiettekatte F and Terreault B 2008 Appl. Surf. Sci. 255 63
[20] Yamauchi J, Aoki N and Mizushima I. 1997 Phys. Rev. B 55 R10245
[21] Uedono A, Suzuki T, Nakamura T, Ohdaira T and Suzuki R 2007 Jpn. J. Appl. Phys. 46 1938
[22] Mantl S and Trifishäuser W 1978 Phys. Rev. B 17 1645
[23] Onishi T, Mizuno M, Fujikawa T, Yoshikawa T, Munemasaj, Mizuno M, Kihara T, Araki H and Shirai Y 2011 J. Electro. Mat. 40 1384