



Density functional theory calculations for estimation of gettering sites of C, H, intrinsic point defects and related complexes in Si wafers



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ABSTRACT

Very recently, a C_3H_5 cluster ion implantation technique for proximity gettering has been reported with the low energy of around $10^{15}/cm^2$ dose without recovery heat treatments. The main feature of this technique is that the gettering efficiency is higher than that by C monomer implantation, even though irradiation defects are too small to clarify by TEM observation. In the present work, we evaluate the binding energies of metal atoms with candidate gettering sites of C, H, intrinsic point defects and related complexes in Si wafers induced by C_3H_5 cluster ion implantation or different methods, for example, H implantation etc. by using density functional theory calculations. In addition to C and H atoms, we consider donor P and O atoms contained in an n-CZ-Si wafer for use in a CMOS image sensor. The simplest complexes of substitutional/interstitial C (C_s/C_i), H_i , P_s , O_i , and incorporated intrinsic point defects (vacancy (V) and self-interstitial Si (I)) by C_3H_5 implantation were also considered. We found that C_s-I ($= C_i$), C_i-C_i , H_i-I , VH_n ($n=1-3$), and VO complexes are the best candidates for gettering sites. Gettering by C_3H_5 cluster ion implantation is more effective than that by C monomer implantation due to the formation of VH_n ($n=1-3$) and H_i-I complexes, which provides more effective gettering sites.

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1. Introduction

There is an increasing demand for “impurity gettering” technology for removing metal impurities from the LSI active region [1]. One of the required devices for gettering is Complementary Metal Oxide Semiconductor (CMOS) image sensors. In the process of manufacturing these sensors with 300-mm-diameter Si wafers, lower and shorter heat treatments make it difficult to apply the internal gettering (IG). This is due to the suppression of nucleation and the growth of bulk micro defects (BMD), such as oxide precipitates and secondary defects. The thinning of the Si wafer in the post-process of semiconductor manufacturing also reduces IG sites for metal impurities. Therefore, proximity gettering techniques by using ion implantation are being considered [2].

For CMOS image sensors, higher-energy carbon (C) monomer implantation had been considered for proximity gettering technology for n/n- epitaxial wafers [2]. However, heat treatments for recovery to reduce defects induced by ion implantation are necessary, and this increases the costs of wafer manufacturing. Very recently, a C_3H_5 cluster ion implantation technique with a low energy of around $10^{15}/cm^2$ dose without the need for recovery

heat treatments has been reported [3]. The main features of this technique are that (1) implanted C and H exist in a window of about 0.1 μm just below the epitaxial layer, (2) the irradiation defects in this window are too small to clarify by TEM observation, (3) oxygen (O) atoms out-diffused from a Czochralski (CZ) Si substrate are gettered in this window, and (4) Fe, Cu, and Ni can be gettered in this window. Clarification of the gettering sites by C_3H_5 cluster ion implantation is important if we want to use this technique in the stable mass-production of CMOS image sensors.

In the present work, we evaluated the binding energy of metal atoms with the candidate gettering sites of C, H, intrinsic point defects and related complexes in Si wafers induced by C_3H_5 cluster ion implantation or different methods, for example, H implantation etc. by using density functional theory (DFT) calculations [4]. We also considered donor P and O atoms contained in the n- wafer which is mainly used for CMOS image sensors. The simplest complexes of substitutional/interstitial C (C_s/C_i), H_i , P_s , O_i , and incorporated intrinsic point defects (vacancy (V) and self-interstitial Si (I)) by C_3H_5 implantation are also considered. The gettering of 12 kinds of metal atoms (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Hf, Ta, and W) relevant to LSI processes is systematically investigated. Various complexes and related clusters which are not considered in this study are presumed to be generated by the C_3H_5 cluster ion implantation. The effect of metal impurity gettering due to such

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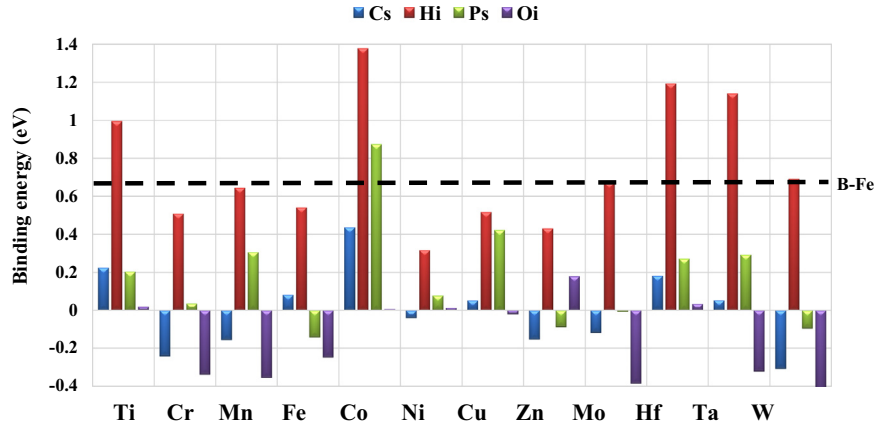


Fig. 1. Binding energies E_b of Cs, Hi, Ps, and Oi atoms to the metals under consideration.

Table 1

Calculated E_b of D–D, D–I, and D–V complexes (eV).

	C _s	C _i	H _i	O _i	I	V
C _s	–1.18	–0.25	1.01	–0.62	1.56 (C _i)	0.39
C _i		1.45	1.75	0.15	1.82	→C _s
H _i			0.98	0.35	0.65	1.93
O _i				0.43	0.22	1.45

complexes and related clusters is, however, beyond the scope of this paper.

2. Calculation details

The method of calculation we used was first principles calculation based on DFT and the pseudopotential [5]. CASTEP [6] was used as the program package. The ground state of the system in this method was found by solving the Kohn–Sham equation, which was a rule equation of the electronic system for a given atom placement. The wave function was expanded as plane waves and the ultrasoft pseudopotential was used to reduce the plane wave number [7]. The cutoff energy for the plane wave expansion was 340 eV. Generalized gradient approximation (GGA) was used for the exchange correlation term and the functional form was of the Perdew–Burke–Ernzerhof (PBE) type [8]. The density mixing method [9] was used to minimize the energy of the electronic system and we ran the Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimizing structure method [10] to optimize atom placement. k-point sampling is performed at $2 \times 2 \times 2$ special points in a Monkhorst–Pack grid [11]. A Si 64-atom cubic cell, i.e., a $2 \times 2 \times 2$ supercell constructed from a conventional cell, was used in this study. The cell was surrounded by (100), (010), and (001) planes and each edge of the cell was along the [100], [010], or [001] direction. Three-dimensional periodic boundary conditions were set for each calculation.

In addition to C and H atoms, we considered donor P and O atoms contained in an n-CZ-Si wafer for the CMOS image sensor. Furthermore, not only these elements but also the simplest complexes with incorporated intrinsic point defects (vacancy (V) and self-interstitial Si (I)) were considered, i.e., four elements D (C, H, P, and O) at (1) substitutional site (D_s), (2) interstitial site (D_i), (3) the D_s–D_s complex, (4) the D_s–D_i complex, (5) the D_i–D_i complex, (6) the D_s–V complex, (7) the D_i–V complex, (8) the D_s–I complex, and (9) the D_i–I complex for the gettering sites. For VH_n and VO_i complexes, we considered VH_n ($n=1-4$) and VO ($n=1, 2$), respectively. The stable structures (and their energies) including

Table 2

Calculated E_b of VH_n + H_i → VH_{n+1} ($n=1-3$) and VO + O_i → VO₂.

Reaction	Binding energy E_b (eV)
VH + H _i → VH ₂	2.03
VH ₂ + H _i → VH ₃	2.00
VH ₃ + H _i → VH ₄	2.46
VO + O _i → VO ₂	1.53

interstitial D_i and/or I should depend on their initial structures before geometry optimization. Therefore, we initially arranged D_i and/or I at some tetrahedral (T)-site, hexagonal (H)-site or [110] dumbbell (D)-site, and obtained stable structures as far as we carried out.

The contamination level in recent LSI processes is controlled to around $10^{12}/\text{cm}^3$ at the highest. This level is far less than the concentration of the gettering sites described above. Therefore, we assumed that each metal atom would be independently getterred at a different gettering site.

After picking up stable complexes among D, D–D, D–V, and D–I as gettering sites G_s, we evaluated their gettering efficiencies by calculating the binding energy E_b with interstitial metal M using Eq. (1):

$$E_b = \{E_{\text{tot}}(G_s) + E_{\text{tot}}(M)\} - \{E_{\text{tot}}(G_s M) + E_{\text{tot}}(\text{Si, perfect})\} \quad (1)$$

For example, $E_{\text{tot}}(G_s M)$ here indicates the total energy of the cell including one possible gettering site and one of the 12 metal atoms (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Hf, Ta, W). $E_b > 0$ indicates the formation of the stable complexes. The stable structure for interstitial metal M was obtained with initially arranged at T- or H-sites in Si. For G_sM complex, we initially set metal M at all of the nearest T- or H-sites from G_s and obtained stable structures.

3. Results and discussion

In our previous paper, we showed the calculated results for the E_b of a substitutional boron (B_s) atom to Fe, Co, Ni, or Cu atoms [4]. The E_b values were in quantitative agreement with the other calculations [12] and experimental results [13–16]. It is well accepted that B_s can be effective gettering sites for Fe in Si [1]. Therefore, we use the E_b of B_s for Fe (0.65 eV) as the critical energy for efficient gettering.

First, we considered the mono C, H, P, and O atoms at the most stable site in Si crystal: substitutional C (C_s), interstitial H (H_i), substitutional P (P_s), and interstitial O (O_i) atoms. Fig. 1 shows the

Table 3Calculated E_b of various complexes including C with metal atoms (eV).

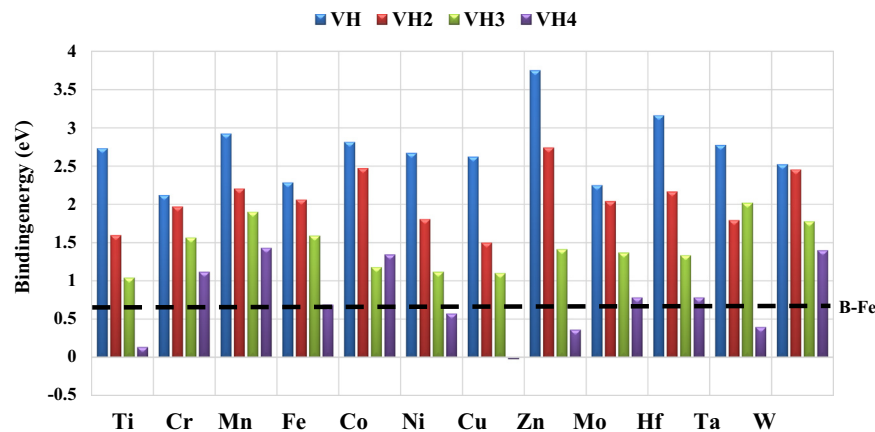
	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Mo	Hf	Ta	W
C _s	0.23	−0.24	−0.16	0.08	0.44	−0.04	0.05	−0.15	−0.12	0.18	0.05	−0.31
C _i –C _i	1.28	0.11	1.22	1.33	1.70	1.46	1.99	1.11	1.04	1.35	0.76	0.57
C _s –I	1.66	0.69	0.77	1.08	0.94	0.84	1.42	0.93	0.60	1.62	1.22	0.81
C _i –I	1.15	0.04	0.31	0.44	0.92	0.49	0.03	0.12	0.49	1.22	0.65	0.62
C _s –V	3.84	2.66	0.90	3.11	3.29	2.77	3.32	4.15	2.75	4.68	3.62	3.19
C _s –H _i	0.96	0.26	0.73	0.51	0.59	0.24	0.68	0.76	0.32	1.17	0.98	0.33
C _i –H _i	1.41	0.67	0.78	1.05	1.12	0.58	1.23	0.98	0.55	1.49	1.07	0.66

Table 4Calculated E_b of various complexes including H with metal atoms (eV).

	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Mo	Hf	Ta	W
H _i	1.00	0.51	0.65	0.54	1.38	0.32	0.52	0.43	0.67	1.19	1.14	0.69
H _i –H _i	1.54	1.25	1.54	0.94	1.62	0.55	0.29	0.42	1.26	1.81	1.50	1.32
H _i –I	2.60	1.92	2.27	1.76	2.10	1.18	1.64	1.64	2.07	3.05	2.80	2.24
VH	2.74	2.12	2.93	2.29	2.82	2.67	2.62	3.75	2.25	3.17	2.78	2.52
VH ₂	1.60	1.97	2.21	2.06	2.48	1.81	1.50	2.74	2.04	2.17	1.80	2.46
VH ₃	1.04	1.57	1.91	1.59	1.18	1.12	1.10	1.42	1.37	1.34	2.02	1.78
VH ₄	0.13	1.12	1.43	0.69	1.35	0.57	−0.02	0.36	0.79	0.78	0.40	1.40
H _i –C _s	0.96	0.26	0.73	0.51	0.59	0.24	0.68	0.76	0.32	1.17	0.98	0.33
H _i –C _i	1.41	0.67	0.78	1.05	1.12	0.58	1.23	0.98	0.55	1.49	1.07	0.66

Table 5Calculated E_b of various complexes including O with metal atoms (eV).

	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Mo	Hf	Ta	W
O _i	0.02	−0.34	−0.36	−0.25	0.01	0.01	−0.02	0.18	−0.39	0.03	−0.32	−0.44
O _i –O _i	−0.02	−0.20	−0.18	−0.37	0.02	0.04	−0.11	0.03	−0.03	0.00	−0.44	0.09
VO	2.20	1.70	1.97	1.75	1.93	1.53	1.48	2.94	1.85	2.59	2.26	2.18
VO ₂	1.72	0.87	1.17	0.74	0.98	0.58	0.51	0.98	0.92	1.35	1.06	1.19

**Fig. 2.** Binding energies E_b of VH, VH₂, VH₃, and VH₄ complexes to the metals under consideration.

E_b of C_s, H_i, P_s, and O_i atoms to the metals in consideration. We found that these four elements are not themselves efficient gettering centers for Fe, Cu, and Ni, which indicates that the gettering sites introduced by the C₃H₅ cluster ion implantation technique are not C_s, H_i, P_s, and O_i atoms themselves.

The window of the proximity gettering region in which implanted C and H atoms with a dose of $10^{15}/\text{cm}^2$ exist is about $0.1 \mu\text{m}$ [3]. This indicates that the concentrations of C and H atoms in this window are around $10^{20}/\text{cm}^3$, which is about $10^5/\text{cm}^3$ larger than the donor P_s atoms of n- substrates. The concentration of captured O_i atoms out-diffused from Si bulk is also far larger than that of P_s. Therefore, the number of complexes including P_s atoms is probably negligible compared to those including C, H, and O

atoms.

Table 1 summarizes the binding energies E_b of D–D, D–I, and D–V complexes. The contamination level in recent LSI processes is controlled to around $10^{12}/\text{cm}^3$ at the highest. In the case of Ni contamination, for example, Ni atoms with this level are super-saturated around 450°C and are gettered at lower than this temperature. Stable oxygen dimers form at these temperatures with E_b of O_i and O_i (0.43 eV). Therefore, we deem the formation of stable complexes with $E_b > 0.5$ eV in this table as gettering temperatures. We also calculated the E_b of $\text{VH}_n + \text{H}_i \rightarrow \text{VH}_{n+1}$ ($n=1-3$) and $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$, as shown in Table 2. Stable complexes can be summarized as follows.

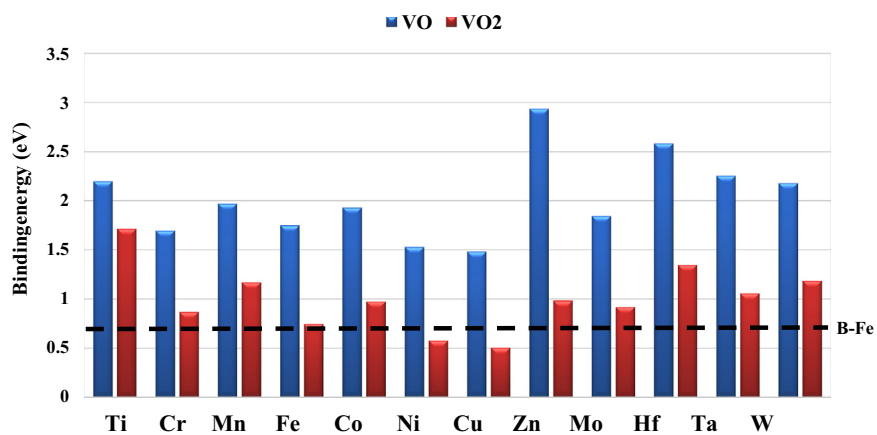


Fig. 3. Binding energies E_b of VO and VO₂ complexes to the metals under consideration.

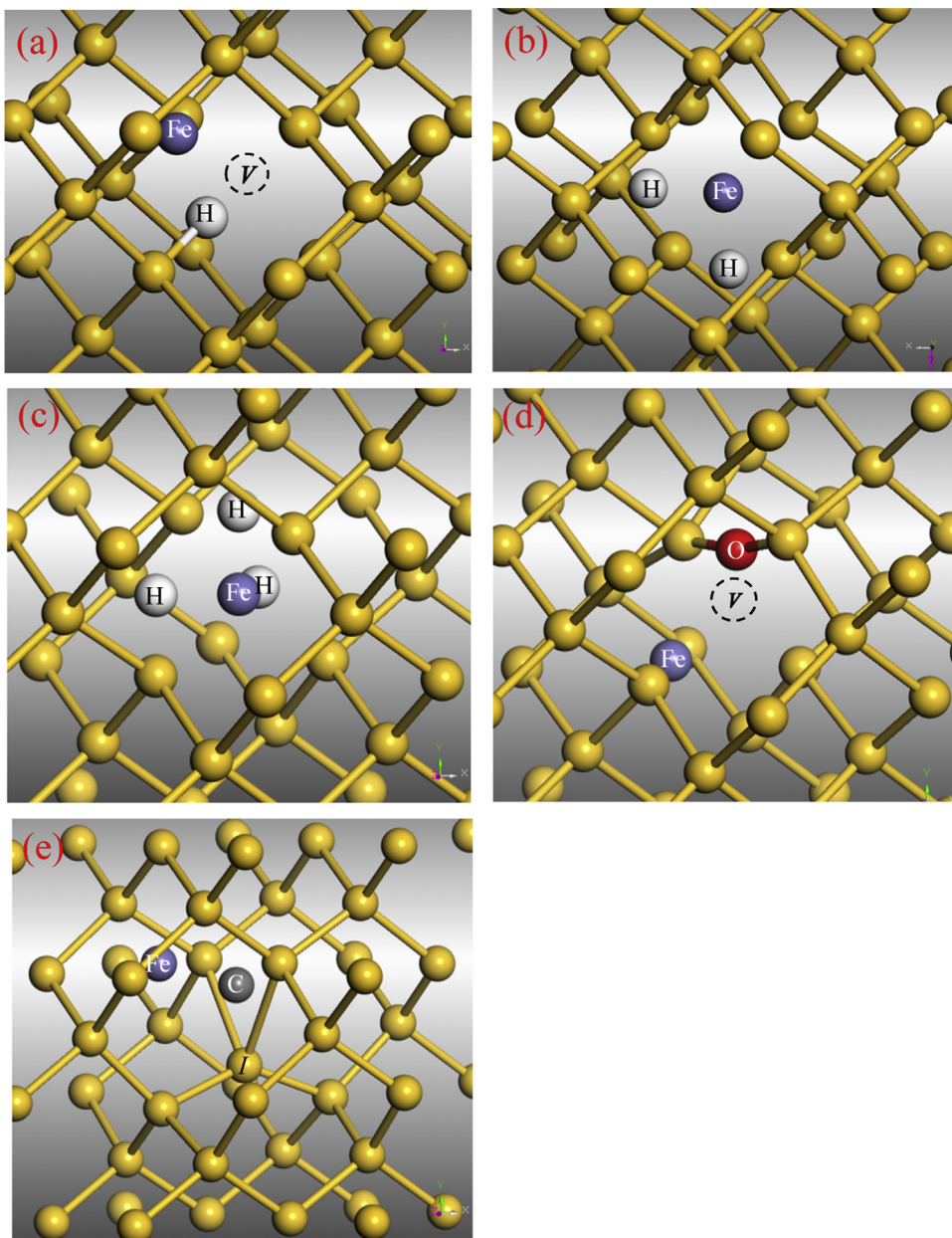


Fig. 4. The stable configurations of Fe atom gettered by (a) VH, (b) VH₂, (c) VH₃, (d) VO, and (e) C_s-I (= C_i) complexes.

1. One element complex (C, H, O)
 C: C_s-I ($= C_i$), C_i-C_i , C_i-I
 H: H_i-H_i , H_i-I , H_i-V (VH), VH_2 , VH_3 , VH_4
 O: O_i-V (VO), VO_2
2. Two elements complex (C, H, O)

C–H: C_s-H_i , C_i-H_i

In terms of intrinsic point defects, vacancy V has the higher E_b with H_i and O_i atoms while self-interstitial I has the higher E_b with C_s and C_i .

Tables 3–5 summarize the database of obtained binding energies E_b for various complexes including C, H, and O, respectively, with metal atoms. The possible complexes by C_3H_5 cluster ion implantation can be deduced from Tables 1 and 2. We determined the effective gettering site with $E_b > 0.65$ eV (B_s –Fe binding energy) using Tables 3–5 by taking all the possible complexes into consideration. A comparison of the gettering experimental results of Fe, Ni, and Cu showed that the C_s-I ($= C_i$), C_i-C_i , H_i-I , VH_n ($n=1-3$), and VO complexes are the strongest candidates for gettering sites introduced by the C_3H_5 cluster ion implantation technique.

To discuss the gettering mechanism behind VH_n ($n=1-3$) and VO complexes, we again summarize the calculated E_b in Figs. 2 and 3, respectively. It is clear that the E_b to metal atoms decreases with increasing H atoms in VH_n complexes. For VH_4 complex, the gettering effect is not sufficient, as E_b for some metals is less than 0.65 eV (B_s –Fe binding energy). These results are probably due to the decrease of dangling bonds with an increase in the n of VH_n , which are active to capture the interstitial metal atoms. In VH_4 complex, no dangling bonds remain. For VO_n complex, one O_i atom terminates two dangling bonds in one vacancy. Therefore, the gettering effect by VO_2 is rather small compared to VO complex. It is also interesting that C_s itself cannot be an effective gettering site but that C_s-I ($= C_i$) and C_i-C_i complexes can. There might be several stable configurations of a metal atom gettering by the proposed gettering sites. The stable configurations of a Fe atom gettering by VH_n ($n=1-3$), VO, and C_s-I ($= C_i$) complexes obtained in the present study are shown in Fig. 4. While the Fe atom is located at the interstitial site in the case of VH or VO complex, the Fe atom seems to move to the substitutional site after gettering by VH_2 or VH_3 complex. Focusing of the relative position between the Fe and the H/O atoms, while the Fe atom is located in the vicinity of the H atom in the case of Fe–VH complex, the Fe and O atoms in Fe–VO complex are separated by the vacancy.

Finally, we briefly discuss the experimental results on the basis of our calculations. The C_3H_5 cluster ion implantation technique provides a better gettering effect than C monomer implantation [3]. Among the candidate gettering sites of C_s-I ($= C_i$), C_i-C_i , H_i-I , VH_n ($n=1-3$), and VO complexes we proposed, neither the VH_n ($n=1-3$) nor H_i-I complexes could be formed by C monomer implantation. This demonstrates that the merit of the C_3H_5 cluster

ion implantation technique is that it can introduce more gettering sites, especially VH_n ($n=1-3$) and H_i-I complexes, that provide a better performance for Si wafer in CMOS image sensors.

4. Conclusion

We evaluated the binding energies of metal atoms with candidate gettering sites of C, H, intrinsic point defects and related complexes in Si wafers induced by C_3H_5 cluster ion implantation or different methods, for example, H implantation etc. by using DFT calculations. In addition to C and H atoms, we considered donor P and O atoms contained in an n-CZ-Si wafer for use in a CMOS image sensor. The simplest complexes of substitutional/interstitial C (C_s/C_i), H_i , P_s , O_i , and incorporated intrinsic point defects (vacancy (V) and self-interstitial Si (I)) by C_3H_5 implantation were also considered. We found that C_s-I ($= C_i$), C_i-C_i , H_i-I , VH_n ($n=1-3$), and VO complexes were the best possible candidates for gettering sites. The reason C_3H_5 cluster ion implantation was more effective for gettering than C monomer implantation is due to the formation of VH_n ($n=1-3$) complexes, which provide more effective gettering sites.

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