NITROGEN-OXYGEN COMPLEXES IN
SILICON AND THEIR DONOR ACTION[①]

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ABSTRACT The electronic characteristic of nitrogen-doped CZ silicon is completely different from that of nitrogen-doped FZ silicon and nitrogen-undoped CZ silicon . It has been found that nitrogen-doped CZ silicon can generate a kind of nitrogen related new donor which forms and disappears with the formation and disappearance of nitrogen-oxygen complexes respectively . The relationship between the formation and disappearance of nitrogen-new donor and annealing condition was studied , and the experimental results were discussed .

Key words nitrogen-oxygen complexes   nitrogen-new donor   CZ silicon

1   INTRODUCTION

In recent years , the nitrogen behavior in silicon has attracted great interest of the researchers . There are two reasons , one is that the research of CZ single crystal silicon under nitrogen atmosphere is successful and CZ single crystal silicon has been put into production , which has broad application prospects ; the other is that studying nitrogen behavior is helpful to deeply study carbon and nitrogen behavior in silicon and their interaction , thus announcing the essence of thermal donor and new donor which has been debating for decades .

In 300 ℃ to 500 ℃ thermal history , oxygen in silicon can generate thermal donor (TD)[1] , making the drift of material resistivity . TD can be annihilated from CZ silicon after annealing at 650 ℃ for 20 min under Ar atmosphere . But for CZ silicon grown under nitrogen atmosphere , material electrical properties have changed a lot because of the involvement of nitrogen . Yang Deren[2] found that for the nitrogen-doped CZ silicon (NCZSi) which has been through resistivity stabilized treatment at 650 ℃ , the resistivity of N-type silicon specimen increases and the resistivity of P-type silicon specimen decreases during the continued annealing above 800 ℃ . Yang Deren[2] concludes that it is due to the formation of TA in NCZSi . Zhang Xiwen[3] indicates that there generates a kind of TD in NCZSi , whose disappearance is related to the resistivity increase of N-type silicon specimen and decrease of P-type silicon specimen .

Nitrogen atoms exist in silicon as N-N pairs , only a small fraction(< 1 %) of nitrogen exists as substitution nitrogen , the nitrogen in FZ silicon hardly has electrical activity . This paper makes detailed discussion in order to make clear the source and essence of nitrogen electrical activity and its formation and disappearance .

2   EXPERIMENTAL METHOD AND RESULTS

2 .1   Electrical properties of minute nitrogen-doped silicon

The experiments were carried out at the same crystal grower (860-D) with a same growing process to obtain nitrogen-doped CZ silicon (NCZSi) and nitrogen-undoped CZ silicon (ACZSi) . The whole procedure for ACZSi is under argon atmosphere , but for NCZSi which is melted under argon atmosphere and grown under nitrogen atmosphere , there is minute nitrogen in

silicon . In the experiment , resistivity of specimen was measured by the four-point probe method , then was converted into carrier concentration as per AST M F723 - 88 , and interstitial oxygen , substitution carbon and nitrogen pairs concentrations were measured by Fourier transmission infrared spectrometer (FTI R) model Nicolet 410 . Conversion is as per GB1551 - 89 , i .e . [O_i] = 6 .28 a_{max}(1 107 c m^{-1})/10^{-6} , [C_s] = 2 .0 a_{max}(607 c m^{-1})/10^{-6} , [N_p] = 3 .66 a_{max} (963 c m^{-1})/10^{-6} .

As grown specimens cut from the tail ends of both N-type ACZSi and N-type NCZSi with 4 m m in thickness have similar oxygen concentration and carbon concentrations less than 0 .1 × 10^{-6} . The specimens were repeatedly annealed for 1 h from 600 ℃ to 700 ℃ , then to 800 ℃ , then back to 700 ℃ , finally to 600 ℃ . After every annealing , the specimens were pulled out from the furnace , quickly cooled down to room temperature , and then cleansed by H F for removing oxide film , finally their resistivity and FTI R were measured . Fig .1 shows the relationship between the resistivity of NCZSi and annealing time , where the number beside each spot represents the number of total annealing hours . From Fig .1 it can be seen that after annealing for 1 h at 600 ℃ , the resistivity of as grown NCZSi falls down while the resistivity of ACZSi increases . During the following annealing , the resistivity increases along with the rise of annealing temperature and decreases with temperature falling down . In its initial annealing phase , this change is reversible . But with the annealing time increasing , the changeable range becomes smaller , finally reaches stable . Fig .2 is the experimental result for ACZSi , which shows that the resistivity reaches relatively stable after annealing for 1 h at 600 ℃ .

There are two infrared absorption lines for nitrogen pairs in FZSi , Wagner[5] did research work on the infrared spectrum of nitrogen-doped CZSi and found that there existed five accompanying absorption lines nearby the two nitrogen peaks , which were resulted in the formation of N-O complexes in silicon . Qi[6] testified that the transformation of nitrogen pairs and N-O com-
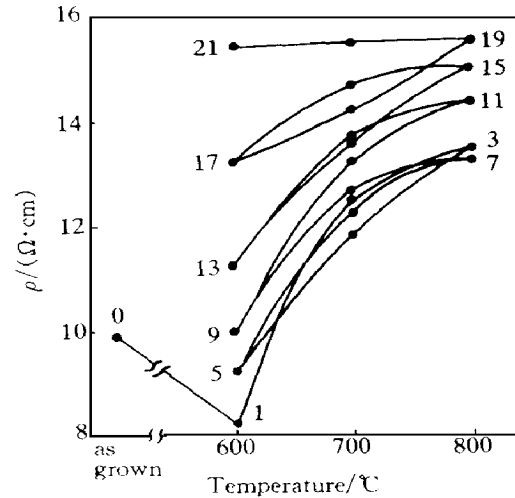
plexes in silicon is a dynamic equilibrium .

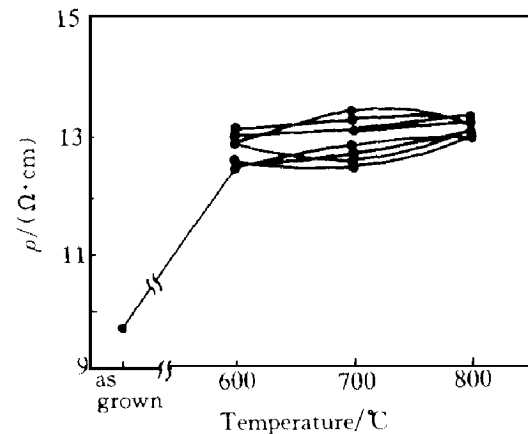**Fig .1**   Relation between resistivity of NCZSi and annealing temperature

Fig .2   Relation between resistivity of ACZSi and annealing temperature

Fig .3 is the infrared spectrum of as grown specimen of NCZSi (spot 0 in Fig .1) , specimen after annealing for 1 h at 600 ℃ (spot 1 in Fig . 1) and specimen after annealing for 1 h at 800 ℃ (spot 3 in Fig .1) . In Fig .3 , NA and NB are isolated absorption lines of nitrogen pairs , NA_1 , NA_2 , NA_3 , NB_1 and NB_2 are absorption lines of N-O complexes . Fig .3 evidences that after the as-grown specimen be annealed for 1 h at 600 ℃ , strength of nitrogen peak decreases while strength of accompanying absorption lines of N-O complexes increases . After the specimen

has been annealed for 1 h at 800 ℃ , the strength of nitrogen peak increases while strength of accompanying absorption lines of N-O complexes decreases . Fig .4 is the variation curve of nitrogen peak strength with annealing temperature and time , which evidences that within 0 ~ 5 h , the variation of nitrogen peak strength with annealing temperature is almost reversible , with the extension of annealing time , shown as spots 1 , 5 , 9 , 13 , 17 and spots 3 , 7 , 11 , 15 in Fig . 4 , both of nitrogen peak strength and strength of accompanying absorption lines of N-O complexes gradually decrease , and then finally
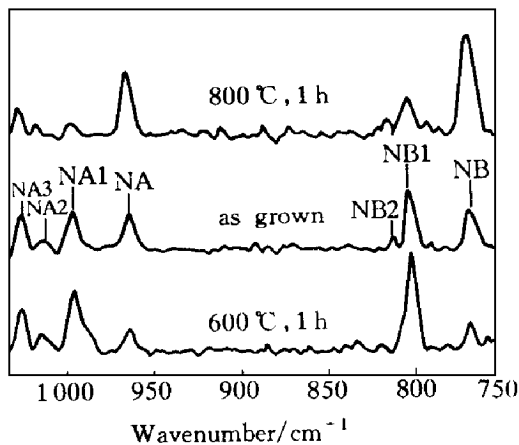

Fig .3 Mutual transformation between nitrogen peak in silicon and absorption line of N-O complexes
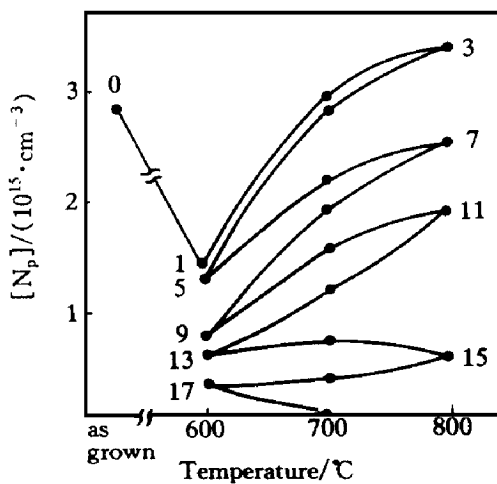

Fig .4 Variation of nitrogen peak strength in NCZSi with annealing condition

disappear .

The resistivity of N-type NCZSi increases , which can be attributed to the formation of TD or the disappearance of original TA . The decrease of N-type NCZSi resistivity can also be attributed to the formation of TA or the disappearance of TD . So the essence of electrical activity of NCZSi only with resistivity variation cannot be explained .

Combining the results of Fig .1 and Fig .4 , it can be seen that when annealing temperature rises , the concentration of nitrogen pairs in silicon increases while the resistivity increases ; when annealing temperature falls down , the concentration of N-O complexes increases while resistivity decreases . If the electrical activity of NCZSi is TA , then when annealing temperature rises , TA is formed and its concentration increases with the increase of nitrogen pairs concentration . If the electrical activity of NCZSi is TD , then when annealing temperature falls down , TD concentration increases , N-O complexes concentration also increase , which evidences that the electrical activity of TA comes from nitrogen pairs , the electrical activity of TD comes from N-O complexes . But it's known to all that nitrogen pairs in FZSi is of no electrical activity , so the electrical activity of NCZSi can only be TD , and this kind of TD is related to the formation of N-O complexes . In order to distinguish between TD and new donor (ND) , it is called Nitrogen-New Donor (N-ND) .

2 .2 Formation and elimination of N-ND

Fig .3 indicates that there exists absorption line of N-O complexes in the as grown specimen , which means that N-ND has been formed in as-grown specimen . Fig .5 shows the relation curve between resistivity and annealing time under different temperature for the specimen cut from the tail of N-type as-grown NCZSi . The experiment indicates that resistivity basically remains the same after 68 h annealing at 650 ℃ , and the specimen maintains N-ND formed in the as-grown specimen ; when annealing time higher than 750 ℃ , N-ND eliminates , the higher the temperature is , the quicker N-ND eliminates ; when temperature is lower than 650 ℃ , N-ND

forms again .

Both of TD and N-ND can be formed after annealing at a temperature lower than 600 ℃ , and it's very difficult to distinguish this two kinds of donor by electrical calibrating , so the experiment used specimens of NCZSi and ACZSi with similar oxygen concentration and thermal history to do comparison tests . The experiment shows that at 450 ℃ , donor concentration of NCZSi increases along with time changing , the reaction rate is lower than that of ACZSi at the beginning , then gradually reaches that of ACZSi . Moreover , infrared measurement indicates that nitrogen concentration remains almost the same during annealing between 0 and 68 h , showing that thermal donor is formed in NCZSi at 450 ℃ , N-ND can be neglected . When at 500 ℃ , donor concentration of NCZSi is higher than that of ACZSi at the beginning and the gap becomes bigger and bigger along with the extension of annealing time , which indicates that both of thermal donor and N-ND can be formed at 500 ℃ . TD cannot but N-ND can be formed at 550 ℃ or 600 ℃ . And at 550 ℃ , the concentration of N-ND is very high .
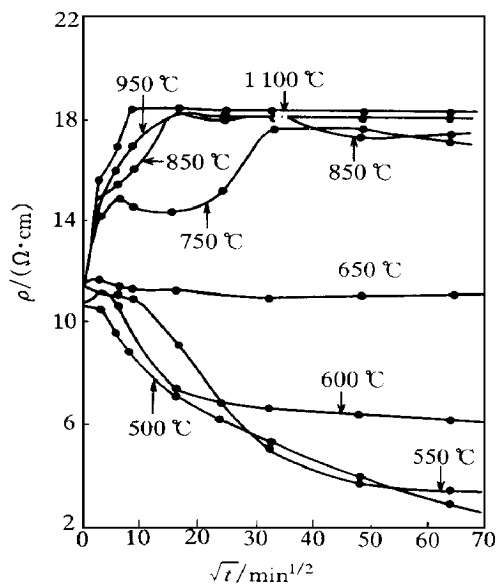
2 .3 Impact of pre-treatment on N-ND

Fig .5   Resistivity of NCZSi variation with annealing condition

Fig .6 shows the variation of donor concentration after annealing for 1 h at 450 ℃ , 1 h at 650 ℃ and 0 .5 h at 1 200 ℃ as pre-treatment respectively . The experiment indicates that the formation speed of N-ND changes a lot after pre-treatment at 450 ℃ or 650 ℃ , but almost has no influence on the balanced concentration of N-ND . On the contrary , the balanced concentration of N-ND decreases obviously after pre-treatment at 1 200 ℃ .
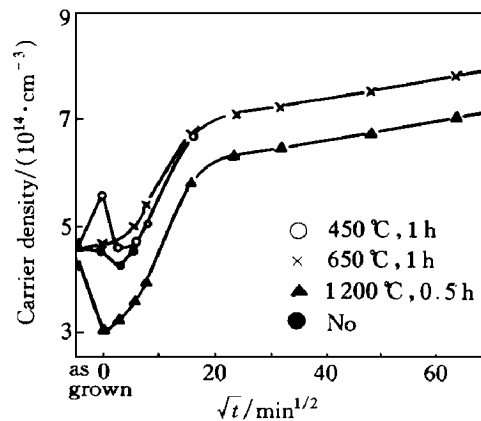

Fig .6   Influence of pre-treatment on N-ND after annealing at 600 ℃

2 .4 N-ND and oxygen precipitates

Fig . 7 shows the variation of interstitial oxygen concentration , nitrogen pairs concentration and carrier concentration with annealing time in N-type NCZSi at 750 ℃ and 1 100 ℃ . In Fig .7 , curve 1 and curve 2 show the variation of interstitial oxygen concentration at 750 ℃ and 1 100 ℃ respectively , curve 3 and curve 4 show the variation of nitrogen pairs concentration at 750 ℃ and 1 100 ℃ respectively , curve 5 and 6 show the variation of carrier concentration at 750 ℃ and 1 100 ℃ respectively .

3 ANALYSIS AND DISCUSSION

The electronic characteristic of nitrogen-doped CZ silicon is completely different from that of nitrogen-doped FZ silicon and nitrogen-undoped CZ silicon . But on the other hand , the infrared research work[5] shows that in the infrared absorption spectrum of NCZSi there exist

5 accompanying absorption lines of N-O complexes near the two nitrogen lines, but no absorption line in the spectrums of nitrogen-doped FZSi or nitrogen-undoped CZSi can be found. This paper directly proves the relation between the formation of N-O complexes and N-ND.
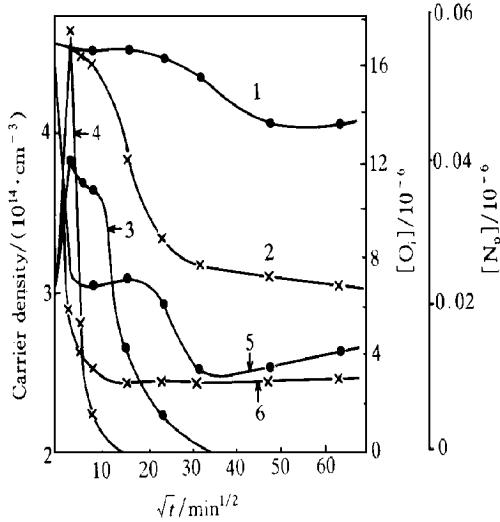

Fig.7   Variation of nitrogen pairs concentration, interstitial oxygen concentration and carrier density in NCZSi with annealing time at 750 ℃, 1100 ℃

There exists a new donor[7] in high carbon specimen, which is related to the formation of C-O complex[8,9]. In the infrared spectrum, C-O complex also have 5 accompanying absorption lines and have a similar structure as N-O complexes[10]. But both of ND and N-ND have donor characteristic with regard to electronic properties, even if being so similar, they are still two kinds of different donors. Their differences are as follows : (1) ND is generated from CZSi with high carbon concentration, there is no ND phenomenon in low carbon specimen, but N-ND is generated from minute nitrogen-doped CZSi; (2) Different formation temperatures, for ND is 500 ℃ to 800 ℃ and for N-ND is 500 ℃ to 650 ℃.

The author thinks[11,12] that N-O complexes in silicon are actually N_2-Si-O complexes. Since the radius of nitrogen atom is small, its electro-negativity is big, nitrogen pairs in silicon

have the ability to attract interstitial oxygen, their interaction generates N_2-Si-O complexes, represented as follows :

N_2-Si tetrahedron + $n O_i$

(N_2-Si_4)

$\longrightarrow N_2$-Si-O complexes

($N_2 Si_4 O_n$)   (1)
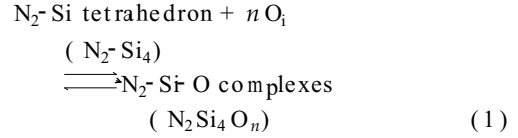
This is a reversible heat emitting reaction of energy decreasing. When temperature falls down, the equilibrium shifts towards the direction of forming N_2-Si-O complexes; when temperature rises, N_2-Si-O complexes dissociate into isolated N-pair and interstitial oxygen[13].

The experiment shows that there is a corresponding relation between N_2-Si-O complexes and N-ND. The bonds of each atom are saturated, the whole complex is electronically neutral. So the complex itself cannot act as N-ND. N-ND may stem from the initial phase of N_2-Si-O complexes dissociating from silicon matrix, which can be expressed as the following reaction :

N_2-Si-O complexes $\xrightarrow{\text{Initial phase of dissociation}}$

N-ND   (2)
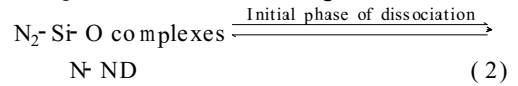
In Fig.4, with the extension of annealing time shown as spots 1, 5, 9, 13, 17 and spots 3, 7, 11, 15, strength of nitrogen peak and absorption lines of N-O complexes gradually decrease and finally completely disappear. Correspondingly, in Fig.1, N-ND concentration also gradually decrease and finally completely eliminates, which evidences that nitrogen in silicon gradually dissociates from matrix, N_2-Si-O complexes which is completely dissociated from matrix not only lose electrical activity, but also lose infrared activity.

N_2-Si-O complexes (N-ND)

$\xrightarrow{\text{Complete dissociation}}$ nuclei center   (3)
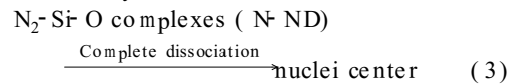
N_2-Si-O complexes which is completely dissociated from matrix act as heterogeneous nuclei center, evidencing the formation of oxygen precipitates.

Nuclei center + $n O_i \xrightarrow{\text{Nucleation and growing up}}$

oxygen precipitates   (4)
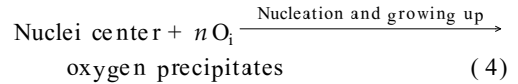
Since dissociation and growing of oxygen precipitates all need active energy, higher temperature is better for reactions (3) and (4) to go

on . The characteristics of N-ND can be well illuminated by analyzing from the above mentioned 4 phases of interaction of nitrogen and oxygen .

In Fig .1 and Fig .3 , when annealing time is not very long , variation of resistivity and nitrogen pairs concentration in silicon are reversible , representing the equilibrium of reactions (1) and (2) . When temperature rises , nitrogen pairs concentration increases , N-ND concentration decreases , resistivity increases . With the extension of annealing time , reactions (3) and (4) continuously go on , nitrogen pairs concentration and N-ND concentration gradually decrease until complete elimination .

In Fig .5 , when temperature is lower than 650 ℃ , reactions (3) and (4) can be omitted . When nitrogen and oxygen in as grown specimens are under low temperature , reaction (1) shifts toward the right . Along with the formation of N-O complexes , the concentration of N-ND increases , while resistivity continuously falls down . And due to temperature effect to equilibrium , the lower the annealing temperature is , the higher the biggest concentration of formed N-ND will be .

After annealing for 0 ~ 68 h at 650 ℃ , the resistivity of specimen is unchangeable , nitrogen pairs concentration in silicon gradually reduces till finally disappears . Because at 650 ℃ , nitrogen and oxygen continuously react and form N-ND , and part of N-ND disappear because of reaction (3) . When the formation and disappearance of N-ND are offset , the N-ND concentration in silicon is stable , but nitrogen pairs concentration continuously decreases because of reaction (1) continuously going on .

Combining the results of Fig .5 and Fig .7 , the variation of nitrogen pairs , interstitial oxygen and N-ND in silicon with annealing time at 750 ℃ are divided into 4 phases . The first phase (0 ~ 9 min) is that nitrogen pairs concentration speedily increases , N-ND concentration falls down , interstitial oxygen minutely changes , which is an equilibrium shifting phase , showing that in as grown specimen , the equilibrium of reaction (1) shifts toward the left at 750 ℃ . The second phase (9 min ~ 9 .5 h) is that nitrogen pairs concentration continuously decreases , N-

ND concentration is almost unchangeable , which is a transition phase ; in this phase , the formation of N-ND[reaction (1)] and the disappearance of N-ND[reaction (3)]are offset . The third phase (9 .5 h ~ 17 .5 h) is that nitrogen pairs concentration reduces to zero , N-ND completely disappears , some interstitial oxygen is eliminated , which evidences that along with nitrogen pairs concentration gradually reducing to zero , the forming speed of N-O complexes in reaction (1) becomes lower and lower . The forming speed of N-O complexes cannot offset the disappearance speed of reaction (3) , finally causing N-ND completely disappear , and some interstitial oxygen eliminates , evidencing this is the nuclei phase of oxygen precipitates . The fourth phase (17 .5 h ~ 68 h) is that neither interstitial oxygen nor resistivity changes a lot , evidencing it's difficult for oxygen precipitates to grow up .

Annealing at 1 100 ℃ , both reactions (3) and (4) change very quickly , so after 0 ~ 9 min the equilibrium shifting , nitrogen pairs concentration and N-ND concentration in silicon speedily fall down to zero within 1 h , and then large amount of interstitial oxygen eliminates , evidencing large amount of oxygen precipitates is formed . When at 850 ℃ or 950 ℃ , the variation of nitrogen pairs concentration , N-ND concentration and oxygen precipitates are between that at 750 ℃ and 1 100 ℃ .

The influence of pre-treatment on N-ND is related to temperature and time . When temperature is not very high and time is not very long , only reactions (1) and (2) can be reversibly transformed with the variation of N pairs . When the followed annealing condition reverses again , the equilibrium density of N-ND keeps unchanged . But annealing at 1 200 ℃ for 0 .5 h causes it very easy for reactions (3) and (4) to go on , a part of N-ND in the specimen transform into nitrogen pairs reversibly , the other part of N-ND transform into minute oxygen precipitates irreversibly , in which the irreversibly transformed N-ND cannot be renewable during the followed annealing , the equilibrium density of N-ND remarkably falls down .
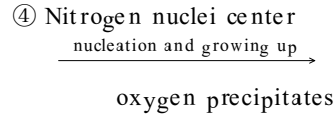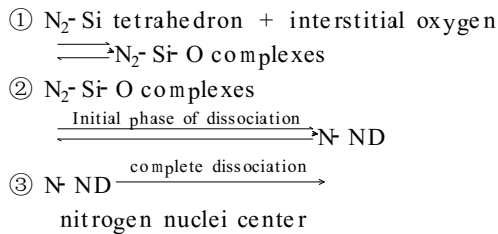
In conclusion , the interaction of nitrogen pairs in silicon and interstitial oxygen can be di-

vided into four phases : (1) Nitrogen pairs and interstitial oxygen interact on each other and form N_2-Si-O complexes ; (2) N_2-Si-O complexes form N-ND in initial phase of dissociation ; (3) N-ND is completely dissociated and new donor annihilates ; (4) The nucleation and growing up of the post dissociation nitrogen center enhance the formation of oxygen precipitates . The influence of annealing condition on the above 4 reactions forms the action of nitrogen in silicon , which can be clearly explained by the experimental results related to nitrogen .

4 CONCLUSIONS

(1) Nitrogen in silicon can form N-ND , which is related to the formation of N-O complexes .

(2) The interaction of nitrogen in silicon and interstitial oxygen can be divided into four phases :

① N_2-Si tetrahedron + interstitial oxygen $\longrightarrow N_2$-Si-O complexes

② N_2-Si-O complexes $\xrightarrow{\text{Initial phase of dissociation}}$ N-ND

③ N-ND $\xrightarrow{\text{complete dissociation}}$ nitrogen nuclei center

④ Nitrogen nuclei center $\xrightarrow{\text{nucleation and growing up}}$ oxygen precipitates

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