Origins of light-induced spin centers in hydrogenated amorphous silicon -nitrogen and silicon-oxygen alloy films

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生年月日	
本籍	中国
学位の種類	博士（学術）
学位記番号	博甲第169号
学位授与の日付	平成８年３月25日
学位授与の要件	課程博士（学位規則第４条第１項）
学位授与の題目	Origins of light-induced spin centers in hydrogenated amorphous silicon-nitrogen and silicon-oxygen alloy films （水素化アモルファスシリコン－窒素及びシリコン－酸素合金薄膜における光誘起スピンセンターの起源）
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学位論文要旨

Under intensive band-gap illumination, it is found that the light-induced spin density increases according to two creation processes, called fast creation process and slow creation process, in a-$Si_{1-x}N_x$:H alloys as well as a-$Si_{1-x}O_x$:H alloys. The experimental results obtained by various methods indicate that there is a large difference in the natures between the spins created in the fast process (FDB's) and the spins created in the slow process (SDB's): (1) the light intensity needed for creating SDB's is far stronger than FDB's, (2) the temperature dependence of the densities are different between FDB's and SDB's, (3) FDB's can be eliminated by sub-gap illumination, but SDB's cannot, (4) attempt-to-anneal frequency ν_0 is $\sim 10^3$ Hz for FDB's and $\sim 10^7$ Hz for SDB's, and (5) the distribution of annealing activation energy (E_A) with two peaks centered at about 0.09 and 0.4 eV for FDB's is in the range from 0 to 0.7 eV, and the distribution of E_A centered at about 1 eV for SDB's is in range of 0.6 $\sim$1.4 eV in a-$Si_{0.50}N_{0.50}$:H sample. All the present results suggest that FDB's and SDB's are formed from different origins, i.e., FDB's an SDB's are associated with a conversion of preexisting charged DB's by capturing photoexcited carries, and generation of new defect, tentatively initiated from a breaking of weak Si-Si bonds, respectively. Parallel investigation shows that the characteristics of FDB's and SDB's in a-$Si_{1-x}O_x$:H are similar to those in a-$Si_{1-x}N_x$:H alloys. For understanding the creation mechanisms of the light-induced ESR spin at low temperature, the dependence of the light-induced ESR (LESR) spins on nitrogen content in a-$Si_{1-x}N_x$:H with a range of x from 0.07 to 0.52 is investigated. The LESR signals for a-$Si_{1-x}N_x$:H samples with $x \leqq 0.50$ are decomposed into three components, D^0, broad and narrow components. An increase in N content influences the spin densities of the D^0, broad and narrow components, as well as the g-values of the D^0 and broad components significantly. Moreover, sub-gap illumination can eliminate the three components. A tentative model is proposed for explaining the present results by comparing the conventional models used for interpretation of the LESR in a-Si:H.

Chapter 1. Introduction

a-Si:H and related alloys have been used extensively in large-area device, microcircuit technology and other device applications, in which the most representative applications are of solar cells, flat-panel displays, photoreceptors, printer heads and thin film transistors, etc. However, a key problem that photoconductivity and dark conductivity is degraded during the procedure of intensive light soaking, which is well known Staebler-Wronski effect (SWE), seriously prohibits the practical application of a-Si:H and related alloys. It was found that the degradation of the conductivity is strongly associated with the creation of light-induced metastable neutral dangling bonds (DB's). In order to reveal the origin of the light-induced metastable defects, the investigation is generally carried out in two aspects: (1) the research on undoped, device quality a-Si:H, using high technique to lessen the influence of impurities as far as possible, and (2) the research on doped a-Si:H or a-Si based alloys so as to explore the influence of adding impurities on the properties of the materials. Although progress in a certain extent has been made within the decades, the key issue, the microscopic mechanism of the photodegradation, is still a mater of debate.

In order to obtain information on the characteristics as well as the creation mechanism of the light-induced metastable spins in a-Si:H and a-Si related alloys, a systematic investigation is carried out by combing studies on creation processes, photobleaching spins using sub-gap illumination, and thermal annealing at various temperatures in Chapters 2-6.

Chapter 2. Creation processes and decay behaviors of light-induced ESR spins in hydrogenated amorphous silicon-nitrogen alloys

The LESR results for strong band-gap illumination for a series of a-$Si_{1-x}N_x$:H samples, such as x=0.32, 0.40 and 0.51, demonstrate that there are two creation processes at both 77 K and room temperature (RT), as shown in Fig.1. as an example for a-$Si_{0.49}N_{0.51}$:H alloy: upon strong band-gap illumination, the spin density increases very rapidly (fast creation process) and become essentially time independent, and after a long time the spin density increases slowly again (slow creation process). We note some differences in natures between FDB's and SDB's. The first is FDB's is far easier created than SDB's. The second is the difference of the the temperature dependence of the density at a given illumination time between FDB's and SDB's, i.e., $\Delta N_{SF}(77K)/\Delta N_{SF}(RT) > 1$, while $\Delta N_{SS}(77K)/\Delta N_{SS}(RT) < 1$. These results suggest that the formations of FDB's and SDB's are related to different creation mechanisms. In addition, a comparison shows that SDB's have the same nature as the photocreated DB's in undoped a-Si:H.

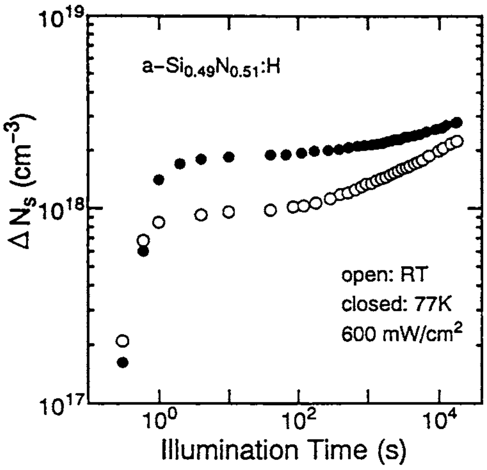

Fig.1. Increment of the spin density as a function of band-gap illumination time in a-$Si_{0.49}N_{0.51}$:H at RT and 77 K.

We also find that the remaining fraction of FDB's after cessation of band-gap illumination is dependent of band-gap illumination intensity (I) and time (t_{ill}), expressed as $N_{ind} = C\, I^{\alpha}\, t_{ill}^{\gamma}$, where C, α and γ are constants for a given sample. The creation mechanisms of FDB's and SDB's are discussed in the late chapters.

Chapter 3. Photobleaching of light-induced ESR spins in fast and slow processes in a-$Si_{1-x}N_x$:H alloys

In this chapter, the photobleaching experiment is mainly aimed at the light-induced DB's in the two different creation processes: FDB' sand SDB's, so as to explore the creation mechanisms. Figures 2(a) and (b) show, respectively, the change in the density in case of only FDB's (illuminated by 600 mW/cm^2 band-gap light for 100 s) and coexistence of FDB's and SDB's (illuminated by 600 mW/cm^2 band-gap light for 5 h) in the sample with x=0.51 in four different treatments: (1) intensive band-gap illumination, (2) decay after cessation of the band-gap illumination, (3) photobleaching by sub-gap illumination and (4) annealing at RT. We find that after sub-gap illumination and RT annealing, FDB's almost completely disappear, while in case of coexistence of FDB' sand SDB's, the remaining density ΔN_2 is equal to the density of SDB's ΔN_1, which suggests that SDB's cannot be photobleached by sub-gap illumination. Moreover, the decrease of the density of FDB's and SDB's under sub-gap illumination can be fit with a stretched exponential function

$$\Delta Ns(t)/\Delta Ns(0) = A + [1-A] \exp[-(t/\tau)^{\beta}], \qquad (1)$$

Where τ and β are dependent of temperature, A a constant.

The present results by comparison with the photobleaching of the photocreated DB's in a-Si:H further indicate that there is difference in natures between FDB's and SDB's. Photobleaching of FDB's suggests that the metastability is the results of carrier capture at preexisting charged DB's, Si_3^- and Si_3^+ during band-gap illumination in analogy with the results for chalcogenide glasses, whose reaction can be written as

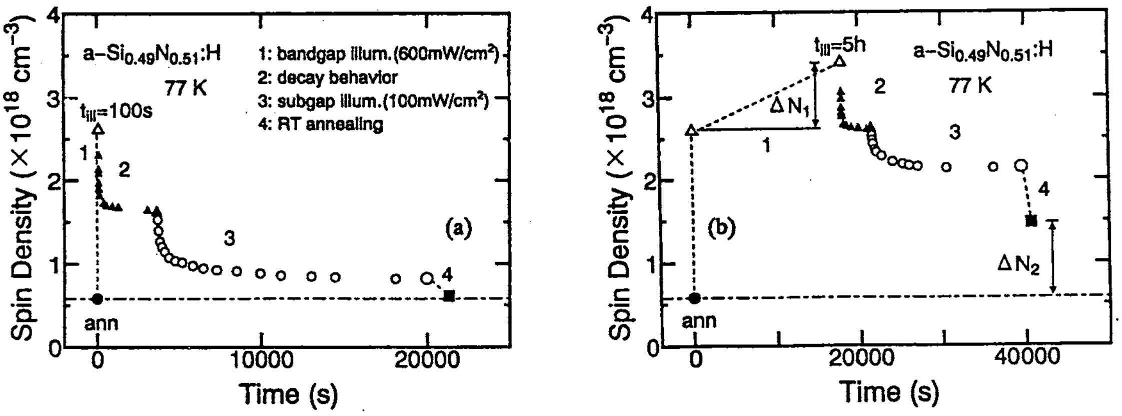

Fig.2. Change in the spin density at 77 K (a) in the case of t_{ill} of 100s (only FDB's) and (b) in the case of t_{ill} of 5h (coexistence of FDB's and SDB's) for a-Si$_{0.49}$N$_{0.51}$:H. ΔN_1 and ΔN_2 indicate, respectively, the net increase of SDB density and the remaining fraction of the LESR spin density after RT annealing.

$$Si_3^+ + Si_3^- \underset{\text{sub-gap ill.}}{\overset{\text{band-gap ill.}}{\rightleftharpoons}} Si_3^0. \qquad (2)$$

Chapter 4. Distributions of thermal-annealing activation energies for light-induced ESR spins in fast and slow processes in a-$Si_{1-x}N_x$:H alloys

We find that the densities of FDB's and SDB's decrease with different annealing behaviors at a given temperature, i.e., FDB's are annealed out far easier than SDB's. Experimentally, attempt-to-anneal frequency, ν_0, for both FDB's and SDB's is determined by decay curves of the densities. ν_0 is ~10^3 Hz for FDB's and ~10^7 Hz for SDB's. By a simulation of the experimental results with the calculated results based on an analysis, we find that FDB's and SDB's are annealed out with distinct distributions of annealing activation energies (E_A's). Figures 3(a) and (b) show the distribution of E_A

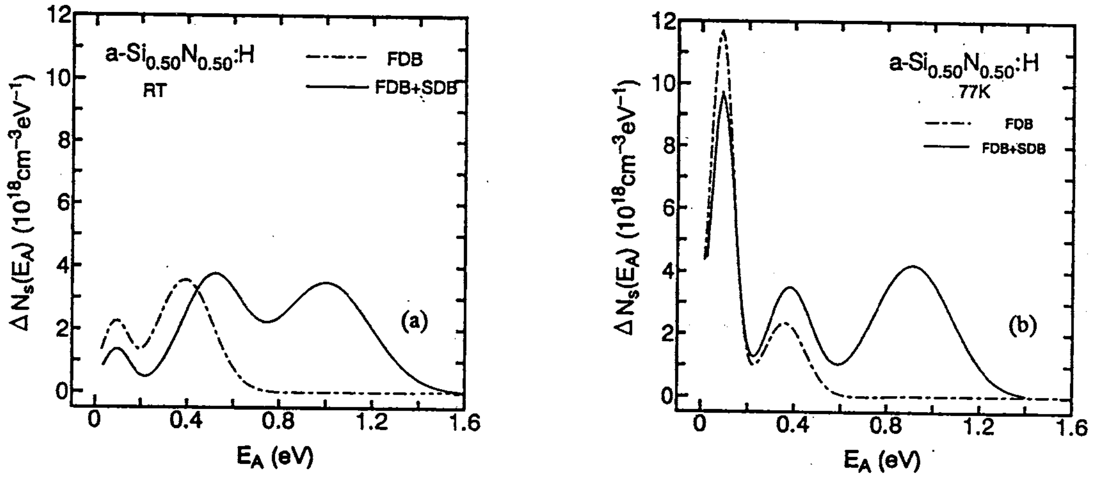

Fig.3. Distributions of E_A for the light-induced spins created at (a) RT and (b) 77 K for t_{ill} of 100s (dot-and-dash curves) and t_{ill} of 5h (solid curves) for a-$Si_{0.50}N_{0.50}$:H.

for the light-induced DB's created by 600 mW/cm^2 for 100 s (only FDB's) and for 5 h (coexistence of FDB's and SDB's) at both 77 K and RT in a-$Si_{0.50}N_{0.50}$:H. One can see that the distribution for FDB's and one for SDB's are separated unambiguously: E_A for FDB's distributes in a range from 0 to 0.7 eV, in which two peaks (centering at about 0.09 and 0.4 eV) are included, and E_A for SDB's distributes in a range from 0.6 to 1.4 eV, centering at about 1 eV. In addition to these, it is demonstrated that the distributions of E_A for FDB's and SDB's depend on illumination temperature and illumination time. Whereas the change tendency of the distributions for FDB's is different from that of SDB's, i.e., with an increase in t_{ill}, the position of the second peak shifts to higher energy, while for SDB's the position of the peak does not change, but the height and the area of the distribution increase. These finding suggests that the difference in distributions between FDB's and SDB's are the results of different creation mechanisms. A comparison indicates that SDB's have a similarity in nature to the photocreated DB's in undoped a-Si:H, such as similar ν_0, the range of E_A and the peak position, suggesting that SDB's are newly created defects, probably by breaking of weak Si-Si bonds.

Chapter 5. Dependence of light-induced ESR spins on nitrogen content in a-$Si_{1-x}N_x$:H alloys

The LESR signals under weak band-gap illumination (6 mW/cm^2) in a series of a-$Si_{1-x}N_x$:H samples with x from 0.07 to 0.52 are measured at 77 K. The LESR signals for the samples with $x \leqq 0.50$ can be decomposed into three components, the D^0, broad and narrow components. As shown in Fig. 4 and Fig.5, the spin densities and the g-values of the D^0, broad and narrow components are dependent of N content: with an increase in N content, the density of the D^0 increases monotonically up to x=0.50, while the densities of the broad and narrow components increase first in the range of $x \leqq 0.32$, and then are almost independent of x for larger x; the g-value of the broad line decreases from 2.01 to 2.006, while the g-value of the narrow keeps at a constant about 2.004. Photobleaching experiment indicates that sub-gap illumination can eliminate the three components. Comparing the conventional models for the explanation of the LESR in a-Si:H, a tentative model is proposed for the interpretation of the present results.

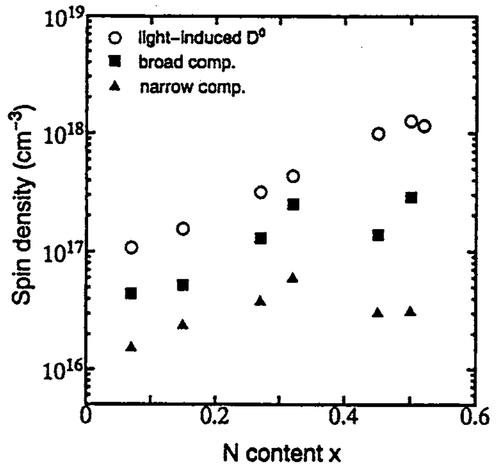

Fig.4. N content dependence of the densities of the D^0, broad and narrow components

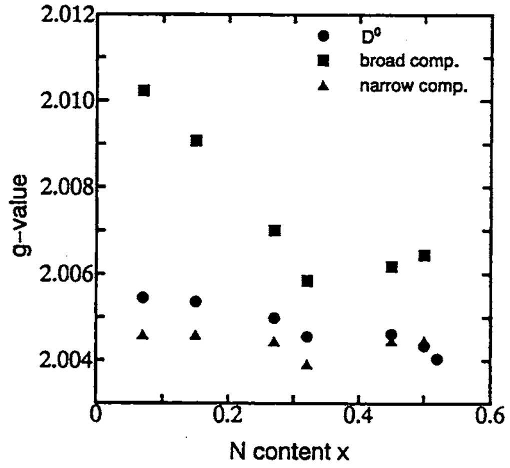

Fig.5. N content dependence of g-values of the D^0, broad and narrow components.

Chapter 6. Observation of two creation processes for light-induced ESR spins in a-Si$_{1-x}$O$_x$:H alloys

In order to explore whether the two creation processes of the light-induced ESR spins are present in other a-Si based alloys, a parallel investigation is carried out for a-Si$_{1-x}$O$_x$:H alloys. We find that two creation processes of light-induced spins are also observed in a-Si$_{1-x}$O$_x$:H alloys under intensive band-gap illumination, and the characteristics of FDB's and SDB's in a-Si$_{1-x}$O$_x$:H alloys are quite similar to those in a-Si$_{1-x}$N$_x$:H alloys. The results indicate that there is a slight difference in g-value between the D^0 at dark, FDB's and SDB's, i.e., the g value of D^0 at dark > the g-value of SDB's > the g-value of FDB's. The decomposition of the LESR signal shows that the decrease of the g-value of FDB's is caused by overlapping of the three components, the D^0, broad and narrow components. It is proposed that the difference in g-value between SDB's and the D^0 at dark is due to that they locate in different regions in which O content is different.

Chapter 7. Concluding summary

Based the present investigation, we conclude as follows:

- Under intensive band-gap illumination, the densities of the light-induced ESR spins in a-Si$_{1-x}$N$_x$:H and a-Si$_{1-x}$O$_x$:H alloys increase according to two creation processes, fast and slow creation processes.
- There are significant differences in the natures between FDB's and SDB's, which are summarized for a-Si$_{1-x}$N$_x$:H alloys as follows:

(1) FDB's are far easier created than SDB's.

(2) The ratio of $\Delta N_{SF}(77K)/\Delta N_{SF}(RT) > 1$, while the ratio of $\Delta N_{SS}(77K)/\Delta N_{SS}(RT) < 1$.

(3) Under sub-gap illumination, FDB's are annihilated, but SDB's are not.

(4) The attempt-to-anneal frequency for FDB's is $\nu_0 \sim 10^3$ Hz, and for SDB's is $\nu_0 \sim 10^7$ Hz.

(5) FDB's and SDB's are annealed according to different distributions of E_A.

(6) The distributions of E_A for both FDB's and SDB's are dependent of band-gap illumination temperature and time. However, with an increase in the illumination time, the distributions of E_A for FDB's and SDB's change differently.

- All of these provide support to that FDB's and SDB's are formed due to two different creation mechanisms: FDB's are formed by a conversion of preexisting charged dangling bonds by capturing photoexcited carriers; SDB's are associated to creation of new defects, possibly initiated from a breaking of weak Si-Si bonds.
- The LESR signals in a-Si$_{1-x}$N$_x$:H samples with $x \leqq 0.50$ are decomposed into three components, the D^0, broad and narrow components, and all the three components can be eliminated by sub-gap illumination. An increase in N content influences not only the densities of the three components, but also the g-values of the D^0 and the broad components.

学位論文の審査結果の要旨

各審査委員による提出論文および関係資料の審査を行い，平成８年１月31日の口頭発表の後，論文審査委員会を開催し協議の結果次の通り判定した。

水素化アモルファスシリコンは，液晶ディスプレーの駆動用薄膜トランジスタや次世代のエネルギー源としての太陽電池などの材料として重要な位置を占めている。しかし，光劣化現象が応用上大きな問題になっている。本論文は a-Si：H の光劣化の原因となる中性欠陥の光生成メカニズムを調べるために，窒素や酸素を添加した水素化アモルファスシリコン系合金薄膜 a-Si$_{1-x}$：H, a-Si$_{1-x}$O$_x$：H において，光誘起スピンの振る舞いを種々の条件で観測し，その起源を明らかにしたものである。

a-Si$_{1-x}$N$_x$：H に対して室温または77K で光誘起スピン密度の時間依存性を丹念に調べると，スピンの生成過程に速いもの（FDB）と遅いもの（SDB）があることが分かる。FDB と SDB の生成過程およびアニール過程には次のような顕著な違いがあることを本論文では明らかにしている。

１． FDB は弱い光でも生成されるが，SDB は強い光で長時間照射が必要である。

２． FDB は室温よりも 77K で生成され易いのに対して，SDB は77K よりも室温で生成され易い。

３．バンドギャップより小さいエネルギーをもつ光（サブバンドギャップ光）を，照射することによって，FDB は減少するが，SDB は変化しない。つまり，FDB には photobleaching が観測されるが，SDB には photobleaching が観測されない。

４．アニールの活性化エネルギーは，FDB に対しては 0-0.7ev, SDB に対しては 0.6-1.4eV に分布している。光照射時間を長くすると，FDB の活性化エネルギーの分布は高エネルギー側にシフトするのに対して，SDB の分布のピークは 1.0eV で一定である。

以上のような実験結果から，FDB と SDB は異なったスピンセンターであることが明らかになった。FDB はもともと試料の中に存在する正と負の荷電した欠陥に光励起キャリアが捕獲されて中性になったものであり，SDB は光照射によって新たに欠陥がつくられるものであると推測している。

このように，異なる生成メカニズムによる光誘起スピンセンターが，同一試料で起こり得ることを明らかにしたことは，種々の試料における欠陥の生成メカニズムを考える上で意義深いことであり，十分に博士論文に値するものと判定される。