PAPER

Hyperfine Structure of Hydrogen Atoms in Hydrogenated Amorphous Silicon

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Abstract

We have observed an ESR spectrum due to atomic hydrogen being composed of a doublet with a splitting of 119 G in a-Si:H samples containing a large amount of hydrogen. Atomic hydrogen is suggested to be located at a tetrahedral-interstitial site either in the bulk region or in the interface between a sample and a substrate.

Key Words: Electron Spin Resonance, Hydrogen, Amorphous silicon.

1. Introduction

It is well known that hydrogen plays an important role in reducing the dangling bond density by terminating dangling bonds in hydrogenated amorphous silicon (a-Si:H)[1]. Hydrogen is bonded to silicon to form Si-H bonds, Si-H_2 bonds, Si-H_3 bonds, (Si-H_2)$_n$ bonds and clustered hydrogen, depending on sample-preparation conditions[1]. A small number of molecular hydrogen has also been observed in a-Si:H[2]. However, atomic hydrogen has not been observed in a-Si:H except in oxygen-doped a-Si:H samples irradiated by x ray at 77 K[3]. In oxygen-doped a-Si:H, two hyperfine lines (hyperfine doublet) have been observed with a splitting of 504 G[3]. For atomic hydrogen in free space, the hyperfine splitting is 506.8 G[4].

In this paper, we report on the observation of hyperfine doublet in a-Si:H samples without x ray irradiation. We discuss the nature of atomic hydrogen responsible for the hyperfine doublet in comparison with the experimental observation of the hyperfine doublet in oxygen-doped a-Si:H irradiated by x ray and the theoretical investigation on atomic hydrogen in crystalline silicon[5].

2. Experimental

The samples used in this study were prepared at 100 °C on fused silica glass substrates by glow-discharge decomposition of mixture gas of SiH_4 and H_2[6]. The values of gas-dilution ratio γ defined by $\gamma = [SiH_4]/([SiH_4 + H_2])$ are given in Table 1 along with the film thicknesses, hydrogen contents, optical gap energies, Urbach tail energies and spin densities. Sample No. 1528 exhibits the peaks of crystalline silicon superposed on the broad peak by amorphous silicon in x ray diffraction patterns, i.e, this sample contains amorphous and microcrystalline phase.

The ESR measurements were carried out at room temperature, using a conventional spectrometer (JEOL JES-RE1X) operating at 9.4 GHz.

3. Results

Figure 1 shows the observed ESR spectrum at a microwave power of 1 mW for sample No. 1538. A strong ESR line is due to dangling bonds, as has already been reported[7, 8]. The two ESR lines observed at the high and low magnetic field sides are identified as the hyperfine doublet due to

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Table 1 Characteristics of samples

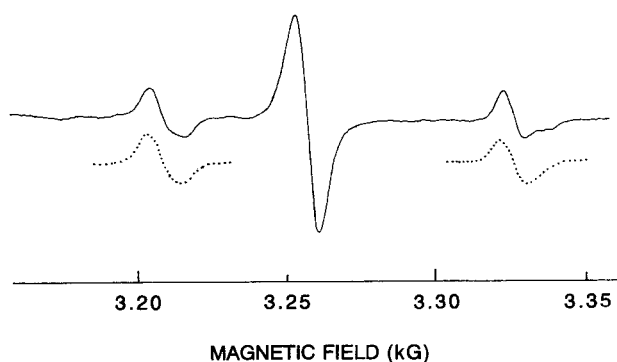| Sample No.	γ (%)	Thickness (μm)	C_H (at.%)	E_{og} (eV)	E_u (eV)	N_s (cm^{-3})
1538	100	1.31	32	1.877	96.1	3.4×10^{18}
1540	50	1.85	26	1.836	83.7	9.7×10^{17}
1541	20	1.30	22	1.830	75.5	1.8×10^{18}
1543	10	1.47	29	1.897	73.8	1.1×10^{18}
1544	5	1.10		1.991	79.6	5.9×10^{18}
1527	3	0.84		2.140	141.8	1.1×10^{18}
1528	2.2	0.78			147.7	4.3×10^{18}

Fig. 1 ESR spectra observed at room temperature for sample No.1538. A main line is due to dangling bonds. Two side lines show the hyperfine doublet. Dotted curves show computer-simulated spectra for the hyperfine doublet.

atomic hydrogen. These components have a structure, being assigned as due to anisotropic g-values. The computer-simulated spectrum obtained using a computer program for nonlinear least square fitting[9] is given in Fig. 1, in which an isotropic hyperfine interaction with a hydrogen nucleus is taken and a Gaussian shape with the standard deviation σ is assumed for the spin packet. The estimated values of g-values with axial symmetry, $g_\parallel$ and $g_\perp$, hyperfine splitting A and standard deviation σ are given by $g_\parallel$ = 1.994 ± 0.001, $g_\parallel$ = 1.999 ± 0.001, A = 119 ± 0.5 G, σ = 4.0 ± 0.5G. The other samples exhibited a similar hyperfine doublet with a splitting of 119 G.

4. Discussion

As mentioned in Section 1, Pontuschka et al.[3] observed the ESR spectrum of atomic hydrogen with a hyperfine doublet of 504 G splitting in oxygen-doped a-Si:H irradiated by x ray at 77 K.

Atomic hydrogen is normally unstable so that it forms a molecular hydrogen by colliding with another atomic hydrogen. Thus, in order to prevent the formation of molecular hydrogen, it would be required to be isolated with one another. As a model for stable atomic hydrogen, Pontuschka et al.[3] suggested that the atomic hydrogen is trapped in an oxygen cage[3], because the signal attributed to atomic hydrogen was observed in oxygen-doped a-Si:H irradiated by x ray at 77 K, but was not observed in undoped a-Si:H samples irradiated by x ray at 77 K under identical conditions. Oxygen seems to stabilize atomic hydrogen in amorphous network of a-Si:H. In the present case, the splitting of hyperfine doublet is much smaller than that of the above case, i.e., in oxygen-doped a-Si:H irradiated by x ray at 77 K. The atomic hydrogen with smaller hyperfine doublet splitting has been predicted by Van de Walle[5] for atomic hydrogen in the tetradedral interstitial (TI) site of crystalline silicon, namely the hyperfine-doublet splitting is 228 G. On the other hand, atomic hydrogen at the bond-centre (BC) site in crystalline silicon exhibits anisotropic hyperfine structure in which isotropic and anisotropic hyperfine interaction constants are -21.3 MHz (-7.61 G) and 25.3 MHz (9.04 G), respectively[5], namely the hyperfine splitting corresponding to separation between two hyperfine lines is 16.6 G. Thus, the hyperfine splitting of 119 G observed in a-Si:H is closer to that for atomic hydrogen at a TI site than to that for atomic hydrogen at a BC site. If amorphous network is taken into account, atomic hydrogen at a TI site in a-Si:H might give a hyperfine splitting of 119 G, namely, its 1s wavefunction extends

more than in crystalline silicon. To stabilize atomic hydrogen at the TI site, however, oxygen is needed in such a way as in x ray-irradiated a-Si:H, O, namely, atomic hydrogen has a few oxygens in neighboring sites opposite to a neighboring silicon. Thus, the overall symmetry of atomic hydrogen at such a TI site may be axial symmetry, being consistent with the symmetry of g-value. Some of the samples exhibiting the hyperfine doublet showed a weak ESR signal due to oxygen-related hole centres[10], particularly at higher microwave powers than 1 mW. This suggests that oxygen is either incorporated into the samples or is in the interface between the sample and the fused-silica substrate. Thus, it is considered that atomic hydrogen at a TI site with oxygen neighbors exists either in the bulk region or in the interface between a-Si:H and the substrate. Further investigations are required to identify the nature of atomic hydrogen and its environment.

5. Conclusions

We have observed a hyperfine doublet due to atomic hydrogen in a-Si:H samples containing a large amount of hydrogen. It is suggested that atomic hydrogen is located at a TI site either in the bulk region or in the interface between the sample and the substrate.

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