CHAPTER VI CHANGES OF MIDGAP STATES

6-1. Introduction

Many techniques, summarized by LeComber and Spear,[1] have been developed to determine a density-of-states distribution [g(E)] in hydrogenated amorphous silicon (a-Si:H), silicon-germanium alloy (a-$Si_{1-x}Ge_x$:H) and silicon-carbon alloy (a-$Si_{1-x}C_x$:H) films, because the electric properties of these films are critically linked with their g(E). All these techniques have some limitations in their application. It is especially difficult to determine the g(E) in highly resistive (e.g., undoped) amorphous semiconductors, but the properties of undoped films usually limit the performance of amorphous devices, such as solar cells and thin-film transistors. Chapters III and V have developed techniques for determining a midgap-state density (N_I) and the g(E) below the Fermi level (E_F) in highly resistive amorphous semiconductors from the high-frequency capacitance of highly resistive amorphous/lowly resistive crystalline semiconductor heterojunction structures, referred to as the heterojunction-monitored capacitance (HMC) method.

Once the g(E) in undoped a-Si:H has been determined, the change of g(E) due to incorporation of Ge or C into undoped a-Si:H is interesting. Furthermore, the changes of g(E) in undoped a-Si:H by light soaking, rapid cooling and thermal annealing are anxious to be surveyed in order to understand the nature of metastable midgap states which has been interesting to researchers both studying the physics of amorphous semiconductors and designing a-Si:H-based devices.

The existence of the light-induced reversible changes in a-Si:H has attracted considerable attention, mostly because of the degradation of the efficiency of a-Si:H solar cells. This effect, which is known as the Staebler-Wronski (S-W) effect,[2] arises from the creation of metastable gap states by light soaking, and it is recovered by the thermal annealing at 150-200 ℃. Stutzmann et al.[3] have proposed the following mechanism;

the rate of increase in dangling bond density (N_S) determined by electron spin resonance (ESR) measurements is given by the relationship that dN_S/dt is proportional to $\Delta n \Delta p$, where Δn and Δp are the free electron and hole concentrations, respectively under light exposure. Each concentration is proportional to G/N_S, where G is the carrier generation rate by light exposure. They have concluded that $N_S(t)$ is proportional to $G^{2/3}t^{1/3}$.

Once N_S has been increased by light exposure, the kinetics of its thermal annealing can be explored. Stutzmann et al.[4] have proposed a monomolecular annealing process with a distribution of activation energies (E_a), while Lee et al.[5] have proposed a bimolecular annealing process with one E_a. Smith and Wagner[6] have expanded the Stutzmann's models for creation and annealing of midgap states into a more general model which can explain the reason why N_S cannot be reduced to the value below 10^{15} cm^{-3} for undoped a-Si:H.

Han and Fritzsche,[7] and Qiu et al.[8] have reported that two kinds of light-induced states are produced by light soaking; one is detected by photoconductivity measurements, and the other is observed by constant photocurrent measurements (CPM). Kumeda et al.[9] have pointed out from the results of ESR that singly-occupied dangling bonds (D^0) created by short-time (3-h) light soaking are easily annealed out, while D^0 created by long-time (53-h) light soaking are resistant to the annealing.

Section 6-2 has applied the HMC method to undoped a-Si:H, undoped a-$Si_{1-x}Ge_x$:H and undoped a-$Si_{1-x}C_x$:H, and discusses the behavior of these midgap states when Ge atoms (or C atoms) are incorporated into undoped a-Si:H. In Section 6-3, the thermal annealing kinetics of midgap states in undoped a-Si:H are investigated, and E_a at each energy position of midgap states (i.e., D^0) is directly determined from the transient HMC method. Since the transient HMC method can obtain the g(E) in a short time (e.g., several seconds), it enables us to carry out the real-time measurements of g(E) in the process of a 150-℃ annealing. In Section 6-4, changes of g(E) in undoped a-Si:H are investigated before and after light soaking, rapid cooling, and thermal annealing by means of the HMC method.