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Internal Friction of Amorphous and Nanocrystalline Silicon Containing Hydrogen

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ABSTRACT

Modern technology requires the increased use of crystalline and amorphous solids in the form of thin films, for example in the field of microelectronics and micro-electro-mechanical systems. Our work has focused on thin silicon films as used for photovoltaic energy conversion. While the electrical and optical properties of these films are known to influence photovoltaic device performance, we have used measurements of the elastic properties to provide a new approach to the study of disorder in these films. The films are deposited on specially shaped double paddle oscillators, which have extremely small intrinsic mechanical damping. The thin films change the oscillators' resonance frequency and damping and from those changes, the elastic properties of the films themselves can be determined [1].

Most of our work is aimed at an improved understanding of hydrogen in amorphous and crystalline silicon films. Hydrogen is essential in making amorphous silicon an electric semiconductor by saturating dangling bonds, but it also causes a deterioration of the photovoltaic conversion efficiency after extended illumination (the Staebler-Wronsky effect). We report on four experimental investigations: atomic hydrogen in amorphous silicon, bulk molecular hydrogen at the interface between amorphous silicon films and the crystalline silicon substrate, hydrogen ion implantation in crystalline silicon, and the search for evidence of bulk hydrogen in microcrystalline silicon films.

1. Atomic Hydrogen in Amorphous Silicon

In concentrations near 1 atomic percent, hydrogen incorporated by the Hot Wire Chemical Vapor Deposition method (HWCVD) has the extraordinary effect of removing practically all low energy localized excitations, usually referred to as tunneling states. These states have been found in all amorphous solids, including films of pure silicon produced by e-beam evaporation and sputtering. The tunneling states lead to a mechanical damping (internal friction) which is independent of temperature, and the magnitude of which is independent of the material - except in the HWCVD films, where their concentration is several orders of magnitude smaller [2]. The non-uniform distribution of hydrogen in these films makes this effect particularly difficult to understand. As the hydrogen concentration increases, the internal friction increases. In films produced by Plasma Enhanced Chemical vapor Deposition (PECVD), in which the hydrogen concentration usually exceeds several at%, the internal friction is also larger, i.e. these films behave more like all other amorphous solids [3]. In order to test whether the small concentration of

hydrogen incorporated during the HWCVD process leads to the vanishing of the tunneling defects, or whether the HWCVD technique itself is responsible, it would be very important to study a-Si produced by sputtering in a hydrogen atmosphere. This process allows the hydrogen concentration to be varied in a controlled way.

2. Bulk Molecular Hydrogen at Interfaces

When a-Si films containing small hydrogen concentrations are deposited or annealed under conditions which allow some of the hydrogen to diffuse, bubbles can form at the interface between the film and the substrate. This bulk hydrogen causes an internal friction peak at 13.8K, the triple point of bulk molecular hydrogen (deuterium results in a similar peak at 18.7K, its triple point) [4]. The characteristic damping extends to below 2K. The same anomaly has also been observed in crushed and hydrogen-loaded steel, where it has been connected to the problem of hydrogen embrittlement [5]. In this case, the anomaly has been explained through dislocation motion during plastic deformation at low temperature, and through atomic migration of hydrogen at grain boundaries close to the triple point. The same anomaly has recently been observed in noble gas films of neon and argon, though only at temperatures low enough to avoid evaporation of the films [6]. From this it follows that plastic deformation by dislocation motion appears to be a common source of internal friction in these cryocrystals. These observations have shown that bulk hydrogen can be detected through internal friction measurements, even at very small average concentrations. It would be very interesting to pursue these studies in bubbles of varying sizes, in particular to determine the limit of the bubble sizes in which bulk behavior can be observed.

3. Hydrogen Ion Implantation

A common method for doping silicon is by ion implantation, and we have used internal friction measurements to explore the disorder it produces and its subsequent annealing. Ion implantation at low doses causes a gradual increase of a temperature-independent internal friction plateau at low temperatures, similar to the one observed in amorphous solids, and a narrow peak centered at 48K. This peak can be described through a single Debye relaxation process with an activation energy of 0.08 eV. The same effects have been observed after implantation with the heavier ions B⁺ [7], Si⁺ [7], and As⁺. By annealing between 200 and 300C, this relaxation peak is removed, while removal of the plateau requires higher temperatures [8]. The relaxation peak has been identified with divacancies, the smallest defects produced by implantation which are stable

at room temperature. Because of their different annealing kinetics, different types of defects must cause the plateau and the 48K peak. Of particular interest is the question whether any connection exists between these defects and the tunneling defects observed in amorphous solids. These findings suggest that internal friction measurements may be particularly well suited for the study of the divacancy depth profile through measurements after gradual removal of the implanted layer by ion-beam etching. Such work would allow us to test the predictions of computer simulations (e.g. TRIM), and to compare our findings with results from positron annihilation studies [9] and from deep level transient spectroscopy [10].

4. Hydrogen in Microcrystalline Silicon Films [11]

These films had been expected to be particularly sensitive to small amounts of hydrogen (especially in bulk form) because pure crystalline films were expected to have negligible internal friction, comparable to that of films grown by molecular beam epitaxy. Much to our surprise, we found that in HWCVD films, the low temperature plateau was large, close to that observed in sputtered a-Si, and that this plateau was entirely independent of the crystalline fraction of the film. No evidence was seen for any bulk hydrogen (at 13.8K), which we had expected to collect between the crystalline grains. Instead, a broad relaxation peak (far broader than a single Debye relaxation) was found around 40K in amorphous films containing more than 10 at% hydrogen. This peak was absent in the crystalline films which had only somewhat smaller hydrogen concentrations (~4 at%). In PECVD films, increasing the crystalline fraction actually *increased* the plateau damping. Again, no hint of bulk hydrogen could be detected. A broad Debye relaxation peak at 60K arose with increasing crystalline fraction, but was absent in the amorphous films. This is the opposite of the behavior seen in the HWCVD films. The origin of these broad relaxation peaks is not known. In conclusion, no evidence for bulk hydrogen has been observed in the microcrystalline films. However, these films show a very large unexpected internal friction plateau, which indicates a disorder as large as in amorphous solids. Its origin is not understood at all, nor is its possible influence on the performance of photovoltaic devices made from such films.

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