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Review

Analysis of semiconductor thin films deposited using a hollow cathode plasma torch

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Abstract

The hollow cathode plasma torch has been used for several years. One of the major applications has been the deposition of dielectric thin films. However, this technique has also been used to deposit metals where high-speed deposition is needed. It has proven to be useful in deposition of coatings onto the inside of substrates of complex shape, high-speed etching, and deposition of thin films at atmospheric pressure. In recent years, we have adapted the technique to deposit high-quality amorphous and polycrystalline semiconducting films. A large variety of measurement techniques have been employed to determine the film properties and the results are reported here.

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Keywords: Thin film semiconductors; Hollow cathode; Sputtering; Optical properties

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1. Introduction

Much of the early work on hollow cathode sputtering was accomplished with the anode within a hollow cathode cylinder, and sputtering was done onto this anode [1,2]. It was later shown that using a hollow cathode with a small inside diameter, a nozzle, rapid deposition of thin films could be accomplished by a plasma chemical vapor

deposition technique (PCVD) using an RF-generated plasma [3,4]. The technique was further developed into a system that could RF reactive sputter deposit thin films onto a substrate placed near the exit of the nozzle; some examples are noted [5–7]. The PCVD process is the only way semiconductor films were deposited using the hollow cathode approach [8] until recently [9–12].

Semiconducting thin films can be grown successfully because of the advantages realized by the hollow cathode method. In addition to the fact that the hydrogenated amorphous silicon, a-Si:H, can be grown without the use of

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silane, the advantage not present in other sputtering techniques is that the intense plasma dissociates the hydrogen gas and it enters the film as an SiH bond, the desired hydride [9]. Similarly, hydrogenated amorphous silicon/germanium, a-SiGe:H, can be grown without silane or germane. The absence of the need for the highly toxic, expensive germane gas is a big advantage of this method. The hydrogen enters the film as a GeH and as an SiH bond, although there are some SiH₂ bonds [11]. The advantage to growing Ge_xC_{1-x} films using the hollow cathode technique is that carbon can enter into the Ge lattice at lattice sites to a greater concentration than can be accomplished using other techniques [12]. Some of the more important results of these experiments are discussed below.

2. Deposition technique

A schematic diagram of the nozzle system used in this research is seen in Ref. [12] (Fig. 1). Each type of material is subjected to different conditions. In the case of the amorphous semiconductors, a-Si:H, a-Ge:H, and a-SiGe:H sputtering is caused by the bombardment of ionized Ar gas. Hydrogen also flows through each nozzle. The purpose of the hydrogen, which dissociates into atomic H in the high-density plasma, is to tie up the dangling bonds of the disordered material. Deposition at a substrate temperature of 230 °C appears to be optimal for this deposition and the H bonds to the Si and Ge at this temperature.

In the case of the polycrystalline Ge_xC_{1-x} films, hydrogen flows through the Ge nozzle, but at the substrate temperature of 350 °C, no H or H_2 remains in the films. The objective of the hydrogen gas is to assist in the crystalline growth of the films. Hydrogen gas did not flow through the C nozzle because the plasma would not ignite or would rapidly extinguish with the flow of hydrogen through the C nozzle. As will be shown, flowing hydrogen only through the Ge nozzle is adequate to achieve the desired results.

An Al impurity was added to some of the more recent films. In order to keep the sputter deposition rate of Al at a much lower level than the Ge or C, Ne gas was added to the Ar flow. The reason for this is that the sputter yield of Ne is much less than that of Ar as a consequence of its smaller mass.

3. Hydrogenated amorphous silicon

The first films were deposited in an ultra-high vacuum system that had the capability of deposition from only one nozzle [9]. The design was improved to include the water-cooling lines, gas admission line, and power input on one flange. The new system is also capable of sputtering from as many as five nozzles [10]. The resulting films deposited with the new design were excellent a-Si:H films. In addition to the Fourier transform infrared spectroscopy (FTIR) data which indicated that the desired SiH bond was predominant, if not the sole silicon—hydrogen bonding

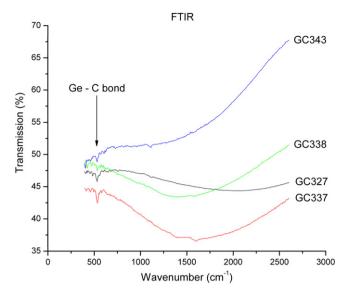


Fig. 1. FTIR curves for four different GeC samples illustrating the presence of the GeC bond at 530 cm⁻¹ and no other absorption peaks.

process, as opposed to SiH_2 or higher hydrides, the light to dark conductivity ratio was excellent for most films grown in this system. The light source for these measurements was an Oriel 75 W xenon arc lamp filtered to simulate the solar spectrum at air mass one (AM1). The amorphous silicon thin films had light to dark conductivity ratios greater than 10^6 with light conductivity in the 10^{-5} S/cm range. The best a-Si:H films have a Tauc bandgap near 1.8 eV with an atomic hydrogen concentration of about 14%. The growth rate was in the $2{\text -}3\,\mu\text{m/h}$ range. Table 1 illustrates the conductivity results for several samples.

4. Hydrogenated amorphous germanium

The a-Ge:H films were grown in the same vacuum system as the a-Si:H films discussed above. The films had Tauc bandgaps that were all very near 1.0 eV. In addition, the incorporation of hydrogen into the films was again almost exclusively in the form of GeH, rather than any other hydride. The deposition rate for the germanium films, at the same nozzle DC power levels as for the silicon nozzles were higher, in the 2–6 $\mu m/h$ range. The light, AM1, to dark conductivity ratio was typically just above 1, with the highest seen in this series of films at a value of 1.18. Thus, pure hydrogenated amorphous germanium is not useful in photovoltaic applications. However, when added to silicon, the situation changes.

5. Hydrogenated amorphous silicon/germanium

It has been well documented that, in order to achieve 15% stabilized efficiency in an amorphous silicon solar cell, a triple-junction amorphous silicon structure is required [13]. Examples of these high-efficiency cells are those described by Deng et al. [14] and Guha [15], which consist of a wide bandgap a-Si:H cell above a mid bandgap

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