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Opportunities for new materials synthesis by hot wire chemical vapor process

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ABSTRACT

Over the last 20 years the hot wire chemical vapor deposition (HWCVD) technique is being explored as an effective alternative to the conventional plasma enhanced chemical vapor deposition (PECVD) for silicon based thin film devices and is claimed to have various advantages. An important point to be appreciated is the mixed nature of the HWCVD process. On one hand it offers all the benefits of being a chemical vapor process and on the other it has the flavor of physical vapor deposition due to the generation of precursors at a line/plane like source (wire array) far away from the substrate albeit with subsequent transport accompanied by secondary gas phase reactions. The possible control over the secondary gas phase reactions gives a unique feature to the HWCVD process. Apart from employing HWCVD for the preparation of a-Si:H and μc-Si:H with high deposition rates we have extended the applicability of the HWCVD to the synthesis of piezoresistive microcrystalline silicon, diffusion barriers of a-SiC:H, silicon nanowires, boron carbide for thermal neutron detectors, stress free a-SiN:H thin films for MEMS devices and metal nano-templates for semiconductor nanowire synthesis. We also established the applicability of HWCVD in surface nano-engineering to incorporate different functionalities (without actually depositing any film) i.e. nano-engineering or nano-modification of the surface to avoid electromigration on low-k dielectric layers and reduce surface defects in crystalline silicon and also bring about nano-crystallization of metallic thin films. Hence I would like to coin a more general nomenclature for this technique and refer to it as hot wire chemical vapor process (HWCVP). This paper discusses the results and outcomes of some of the case studies that we have carried out employing the HWCVP.

1. Introduction

Chemical vapor deposition techniques have undergone a sea change over the last few decades essentially due to the demand for processing new materials, low temperature substrates, complex shapes and large areas, high throughput and improved properties. Plasma enhanced chemical vapor deposition (PECVD) is an outcome of some of the above demands. This technique itself has seen new variants coming in like microwave plasma, pulsed plasma, very high frequency (VHF) plasma, remote plasma and so on [1]. The need for inventing newer techniques is the inability of the existing ones to have all the capabilities that are required for the development of the thin films of the new material systems for various applications. A decoupled CVD process (wherein the deposition zone is separated from the dissociation zone in terms of the temperature and space) is a complicated process where radical generation and recombination (leading to new radicals) compete with each other and one has to strike the right conditions so as to maximize the yield and have the desired film properties.

The advent of the hot wire CVD initially for making diamond like films and then getting extended to the making of silicon based thin films has initiated a large amount of activity with the claims about its potential advantages over the PECVD [2–8]. Many of these claims have also been demonstrated in terms of some process–structure–property related aspects for silicon based materials [9–12]. Being comparatively new the HWCVD (henceforth referred to as HWCVP) [13] is still largely ill-understood and needs huge efforts to be implemented on the industrial scale. There are two important differences when compared to PECVD, a) generation of the radicals in the HWCVP is local and in a plane constituted by an array of filaments (or a line if a single filament is used) of some refractory metal (tungsten or tantalum) a few centimeters away from the substrate and b) there is a unique filament temperature responsible for the dissociation of the precursor gas unlike in PECVD, where the electron impact dissociation is fostered over a large electron energy range and radicals are generated almost over the entire volume of the plasma. Hence, in HWCVP, one expects a more sensitive dependence of the film properties on the secondary gas phase reactions during the transport of the radicals from the source to the substrates. On the other hand, this can be beneficial also in terms of controlling the deposition kinetics and hence achieving the desired film characteristics.

This article describes the results of our attempts to synthesize a-Si:H and μc-Si:H films at high deposition rates, μc-Si:H with high piezoresistivity gauge factor, silicon nanowires and boron carbon alloys by the HWCVP. We have also exploited the HWCVP to form nano-templates of metallic systems which then enable us to grow silicon

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nanowires employing the HWCVP. The HWCVP has been employed to synthesize the thin films of the various materials system keeping in mind the applications. Appropriate precursors were used for this purpose and diluents or carrier gasses were used wherever needed. The films were prepared under different deposition conditions of substrate temperature, filament temperature, distance, pressure, dilution ratio, precursor gas flow rates, etc. Each section mentions the relevant experimental conditions. Details of our HWCVP tool are available elsewhere [14]. Various substrates were employed as required by the characterization technique used. Films have been characterized for their physical, optical and electronic properties.

2. Results and discussion

2.1. Piezoresistive μc-Si:H

Piezoresistance is defined as the fractional change in bulk resistance induced by small mechanical stresses applied to a material and is quantified in terms of gauge factor, which is defined as the fractional change (R/Ro) in the resistance per unit strain (ε) [15],

$$G = (R/Ro)/\varepsilon. \quad (1)$$

This change in resistance arises from two effects:

1. The change in the dimension of the resistor, and
2. The change in the resistivity of the material itself [16].

In semiconductors, the resistivity change is larger than the dimensional change by about a factor of 50 [17]. This change in resistivity is due to the change of the energy gap though to a very small extent. The number of carriers and hence the resistivity therefore changes. Crystalline silicon and poly-crystalline Si made by conventional CVD show large gauge factors. However there is a need for developing thin films with high gauge factor at low processing temperature. There has been a lot of work done in this direction by employing both conventional PECVD as well as the HWCVP deposition technique. Gauge factors of the order of 25 have been achieved in HWCVP p-type μc-Si:H films [18]. However there is a lot yet to be done in terms of getting higher gauge factors and lower substrate temperatures. Hence attempts have been made to synthesize micro-crystalline Si (μc-Si:H) thin films by the HWCVP and study their piezoresistance.

p-type μc-Si:H were deposited using silane (SiH_4) and diborane (B_2H_6) gas mixture under different deposition conditions as mentioned below

H_2/SiH_4 flow = 25–45 sccm
B_2H_6/SiH_4 flow = 0.01
pressure = 70 mTorr
substrate temperature = 150 °C
filament temperature = 1650 °C
filament to substrate distance = 6 cm.

The role of hydrogen in the synthesis of microcrystalline silicon films is quite known. In order to see its effect on the gauge factor we deposited and analyzed the effect of varying hydrogen dilution on gauge factor and other film properties important for sensor applications. Fig. 1 depicts this sample architecture employed for the gauge factor determination. A triangular glass substrate is deposited with p-type HWCVP μc-Si:H films (dark region) patterned in longitudinal (along the length of the triangle) and transverse (perpendicular to length of the triangle). The use of triangular substrates ensures uniform tensile or compressive stress on the films when a force is applied at the free end of the substrate and yields accurate gauge factor values [19]. Metal contacts (transparent squares at the ends of the dark regions) are then deposited through physical masks by vacuum evaporation. Gold wire leads are connected

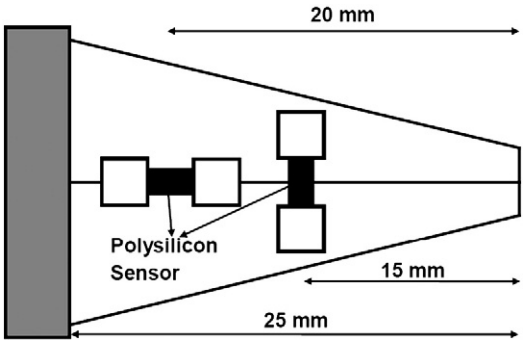

Fig. 1. μc-Si:H films (dark regions) and aluminum pads (white squares) on triangular glass substrate used to measure longitudinal and transverse gauge factor. The left gray region is the clamp to hold the sample rigidly.

to these metal contact pads by silver epoxy. These substrates are mounted on the stage which has a vertical micrometer screw gauge which enables applying controlled force so that the glass substrate can be bent with a known deflection. The leads are connected to a Keithley source meter, which measures the change in the current (for a fixed voltage) as a function of deflection. From this data we calculate the gauge factor.

In order to avoid any temperature effects on the pressure or force measurements, the film material has to have an acceptable temperature coefficient of resistance (TCR). Hence the TCR was determined for the films applicable for piezoresistivity based sensors. This was done by mounting the samples on a stage which had a controlled heating arrangement. The current (for a given voltage) was measured as a function of temperature and the TCR was calculated from this data. Fig. 2 shows the variation of TCR and conductivity (determined by the 4-probe method) as a function of hydrogen dilution for the HWCVP deposited p-type μc-Si:H films. It is seen that as the hydrogen dilution is increased the conductivity increases while the TCR approaches low values. A low TCR indicates a good doping efficiency of the films. The data obtained on our films, clearly indicates that though the TCR values are quite low for the high conductivity films a compensation technique may still be required in an actual device to avoid even the slightest of noise generation due to temperature variations. The above correlation with the conductivity also implies that one needs to strive for the highest conductivity of these films which calls for an efficient doping process. Fig. 3 shows the variation of both the transverse and longitudinal gauge factors under tensile as well as compressive stress for these films. It is seen that the G_{lt} increased from 9.1 to 32.2, while G_{lc} increased from 6.1 to 25.4 as the

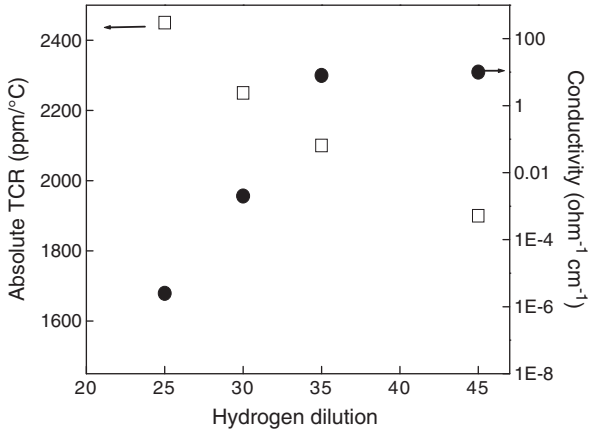

Fig. 2. Variation of temperature coefficient of resistance and conductivity as a function of hydrogen dilution for the HWCVP μc-Si:H films.