CHEMICAL VAPOR DEPOSITION OF CRYSTALLINE AND AMORPHOUS CARBON, SILICON AND GERMANIUM FILMS

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ABSTRACT. The chemical vapor deposition (CVD) of amorphous and crystalline carbon, silicon and germanium films is reviewed. Different deposition methods such as plasma CVD, hot wire CVD and laser CVD are discussed. The chemical mechanisms are considered in detail, including gas phase and surface reactions. Many similarities found for the three systems are pointed out.

1. INTRODUCTION

1.1 Amorphous and Crystalline C, Si and Ge

The elements carbon, silicon and germanium of group IV of the periodic table form well known crystalline phases but also amorphous networks in which the presence of hydrogen is crucial. These hydrogenated amorphous materials a-C:H, a-Si:H and a-Ge:H are of increasing scientific and technological interest. One of the goals of current research in this field is to understand the role played by hydrogen during chemical vapor deposition (CVD) and to elucidate the functions and nature of hydrogen bonding in the covalent solids.

The technique of chemical vapor deposition (CVD) is a non-equilibrium method that allows the synthesis of metastable materials in a wide range of compositions, structures and morphologies. Examples are metastable crystals such as diamond and metastable amorphous solids such as hydrogen alloys. The main attractions of the CVD process are that deposition occurs at relatively low temperatures and pressures and that thin films can be grown on a variety of substrate materials.

In the carbon system an exceptionally large number of crystalline and amorphous structures can be realized due to different types of bonding, namely sp\(^2\), sp\(^3\) and sp hybridization. The current interest concentrates on the sp\(^3\) structures, such as diamond and diamondlike films, which possess superior mechanical, optical and thermal properties. Diamond is a dielectric with a band gap of 5.5 eV, as shown in Fig.1. In amorphous hydrogenated carbon (a-C:H) the band gap is smaller and may vary in a wide range depending mainly on the bonding configuration (sp\(^3\) and sp\(^2\) bonding) [1]. In the amorphous materials the electronic structure usually consists
of σ states from sp³ and sp² bonding and π states from sp² hybridization. The π states lie symmetrically around midgap and define the optical band edges, which depend mainly on the mean size of the sp² clusters [1].

![Band gap of crystalline solids](image)

**Fig. 1** Band gaps of the crystalline solids (C, Si and Ge), the binary hydrogenated amorphous alloys and the ternary amorphous alloys.

Efforts are being made to alloy carbon and silicon in amorphous semiconductors (a-SiC:H) to increase the band gap of a-Si:H as shown schematically in Fig. 1 [2]. Crystalline silicon and germanium are semiconductors with band gaps of 1.14 eV and 0.67 eV, respectively. The transition to the amorphous state is connected with small distortions of the bond length and larger distortions of the bond angle [3]. This destroys the long range order of the crystal lattice, however, the remaining short range order of tetrahedral bonding is sufficient to retain the band structure [4]. In addition, the network distortions create undercoordinated atoms ("dangling bonds"), which increase the density of defect states in the band gap drastically as shown in Fig.2. Incorporation of hydrogen not only improves the electronic properties by saturating dangling bonds but also improves the mechanical properties by stabilization of the overconstrained amorphous network [5]. The electronic properties of hydrogenated amorphous materials are determined not only by the density of gap states but also by the defects at the band edges, the so-called tail states (see Fig.3). It is believed that in a-Si:H and a-Ge:H the thermal and structural network distortions, and thus mainly the deviations in the bond angle may be responsible for the occurrence of the tail states [6]. In these hydrogenated amorphous materials the width of the band gap increases compared to the crystal from 0.67 eV to about 1.1-1.2 eV for high quality a-Ge:H containing 3-