Thin Solid Films 570 (2014) 429–435

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

In-situ doping of erbium in hydrogenated amorphous carbon by low temperature metalorganic radio frequency plasma enhanced chemical vapor deposition

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ARTICLE INFO

Available online 15 February 2014

Keywords:
Erbium metalorganic compound
Hydrogenated amorphous carbon (a-C:H)
Fluorination

ABSTRACT

A significant improvement in the photoluminescence of erbium doped amorphous carbon (a-C:H(Er)) is reported. The effects of the RF power on the anode and cathode a-C:H films were investigated in terms of the microstructural and local bonding features. It was determined that Er doped a-C:H films should be placed on the anode to obtain wider bandgap and lower percentage of sp^2 carbon bonding. The metalorganic compound, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) Erbium(+III) or Er(fod)$_3$, was incorporated in-situ into an a-C:H host by metalorganic rf plasma enhanced chemical vapor deposition. This technique provides the capability of doping Er in a vertically uniform profile. The high erbium concentration (3.9 at.%), partial fluorination of the surrounding ligands, and the large optical bandgap of the host a-C:H are the primary factors that enable enhancement of the photoluminescence.

1. Introduction

The metal-line based electrical interconnections represent the most important limitation on the performance of Si-based microelectronic (CMOS) devices. The delay in the signal propagation arises from several factors including the parasitic capacitances generated at the metal/insulator/metal capacitors, the intrinsic resistivity of the metal lines, and the contact resistance at the metal/metal interface. As device features further shrink, the delay due to the metal interconnection will lead to an unacceptable bottleneck in device performance [1]. A definitive solution is to employ optical interconnects that are able to transfer data at rates that are orders of magnitude above the limit of traditional electronic technologies. These optical interconnects can be inside a Si chip or between chip-to-chip communication. In order to completely avail optical technologies, it is imperative to develop silicon compatible materials which enable light generation, guiding, switching, detection, modulation and amplification. To realize the co-existence of electrical and optical functions inside a Si chip platform, it is crucial to develop compatible photonic materials. These materials must possess processing temperatures below 400 °C, in order to meet the Si back end-of-line (BEOL) requirements for the current integrated circuit (IC) fabrication technology.

The development of Si compatible photonic materials includes the observation of an optical gain in Si nanocrystals [2], electroluminescence for a Si diode [3], Si nanocrystal field-effect-transistors [4], implementation of a Si Raman laser [5], and the realization of a high-speed Si electro-optic modulator [6]. However, given silicon's inherent indirect bandgap, crystalline Si is not able to readily emit light. This limits the approaches described above. Thus the lack of an efficient Si-based light source is self-evident.

Erbium (Er) ion implantation in a variety of Si-based [7–9], silica-based [8,10], and ceramic [8] thin film hosts has a leading role in the effort to efficiently produce photons from Si. The advantage of this approach is that standard Si technology can be deployed to introduce Er as a dopant. In addition, excited Er^{3+} ions emit at 1.5 μm, which is a strategic wavelength for telecommunications due to the minimum in the absorption for silica fibers. However, photoluminescence is severely quenched at room temperature in crystalline Si based hosts [11,12]. Also, co-implantation of additional O atoms is highly preferred in order to reduce Er precipitation and increase the fraction of active Er^{3+} ions [13]. For silica-based and ceramic thin film hosts, a high processing temperature is required to grow good quality material. Also,

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http://dx.doi.org/10.1016/j.tsf.2014.02.038
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high post-annealing temperatures (>700 °C) are typically necessary to eliminate the ion implantation-induced damage, to optically activate the Er^{3+} ions, and/or to enhance the photoluminescence lifetime or quantum efficiency. These high temperature processes are incompatible with Si BEOL fabrication processes.

While research on Er-implanted silicon and silica-based materials has been extensive, Er doping in amorphous carbon based host has received little attention [14–17]. Hydrogenated amorphous carbon (a-C:H) films can be grown by a low-temperature plasma enhanced chemical vapor deposition (PECVD) method. PECVD methods are compatible with current CMOS fabrication technology. They allow ease of integration and reproducible processing, and are low-cost. Furthermore, a-C based films possess a number of outstanding properties such as high chemical resistance, biocompatibility, mechanical hardness, and transparency in the infrared [18,19]. Due to their excellent tribological properties, a-C:H films are widely used as protective coatings for hard disks and magnetic media, machine parts, optical windows and fibers, etc. [20]. In the past few years, a-C:H coatings have been also implemented on biomedical and biosensor products [21]. The specific properties of a-C:H films can be tailored over a wide range by adjusting the sp^3 to sp^2 hybridized carbon ratio, the type of sp^3 (predominately C–C or a mixture of C–C and C–H) and sp^2 (the number and size of the clusters) bonding configurations, and the amount of incorporated hydrogen in the film via various deposition parameters and deposition methods [19].

The first reported demonstration of room-temperature photoluminescence (PL) from Er at 1.54 μm in a-C:H(Er) thin films was published in 2002 [14]. a-C:H(Er) films were deposited by magnetron sputtering of a graphite target that was partially covered by Er platelets in an Ar/C_6H_{12} atmosphere. The Er concentration in the a-C:H(Er) films could be changed from 0.15 at.% to 1.2 at.%. However, the PL intensity was relatively low. This was attributed to the low optical band gap (~0.5 eV) of the sample and the non-radiative relaxation pathway induced by C–H vibrations [15]. In this deposition technique, the Er concentration highly depends on the degree of magnetron sputtering of the Er/graphite target. Accordingly, high Ar ion energy and flux are required to achieve high Er concentration. However, this causes a high concentration of sp^2 carbon and a low optical bandgap. The incorporation of an Er metalorganic compound into a carbon layer by the radio frequency plasma enhanced chemical vapor deposition (RFPECVD) method was demonstrated by Prajzler et al. [16] in 2003. However no PL spectra were presented. In 2009, Tsai et al. [17] grew a-C:H(Er) and a-C:D(Er) films, where D in a-C:D(Er) is deuterium, the isotope of H, via in-situ thermal evaporation of the tris(2,2,6,6-tetramethyl-3-5 heptanedionato) erbium(+III), or $Er(tmhd)_3$, compound in a DC saddle-field PECVD system. A much higher PL signal was obtained from a-C:D(Er) film compared to a-C:H(Er) films. This was due to the optical quenching from the highly abundant C–H bonds. The $Er(tmhd)_3$ metalorganic compound contains a high percentage of C–H bonds, 58.76 at.%. Hence, this precursor is inherently inefficient at promoting Er^{3+} photoluminescence.

In this work, the feasibility of the in-situ growth of metalorganic Er-doped amorphous carbon (a-C:H(Er)) thin films was performed. Films were deposited at low temperature (<200 °C) by a metalorganic radio frequency plasma-enhanced chemical vapor deposition (MO-RFPECVD) system. The properties of the host a-C:H film and the incorporated Er concentration were independently controlled. Prior to the MO-RFPECVD depositions, the effects of the RF power and the placement of substrate in the RFPECVD system were systematically investigated. The structural and optical properties of the host a-C:H material were obtained. These properties were evaluated and discussed with respect to the local bonding features.

2. Experimental details

2.1. MO-RFPECVD and sample preparation

A capacitively coupled MO-RFPECVD system as shown in Fig. 1 was deployed to deposit hydrogenated amorphous carbon (a-C:H) and Er-doped a-C amorphous carbon (a-C:H(Er)) thin films. An ac-powered thermal evaporator was situated next to the RF-powered showerhead electrode (cathode) inside the deposition chamber. The thermal evaporator was used to in-situ dope the Er metalorganic compound while commencing a-C:H film deposition via a methane plasma. A thermocouple was embedded in the external surface of the bottom of the evaporator for feedback temperature control. This measured temperature was

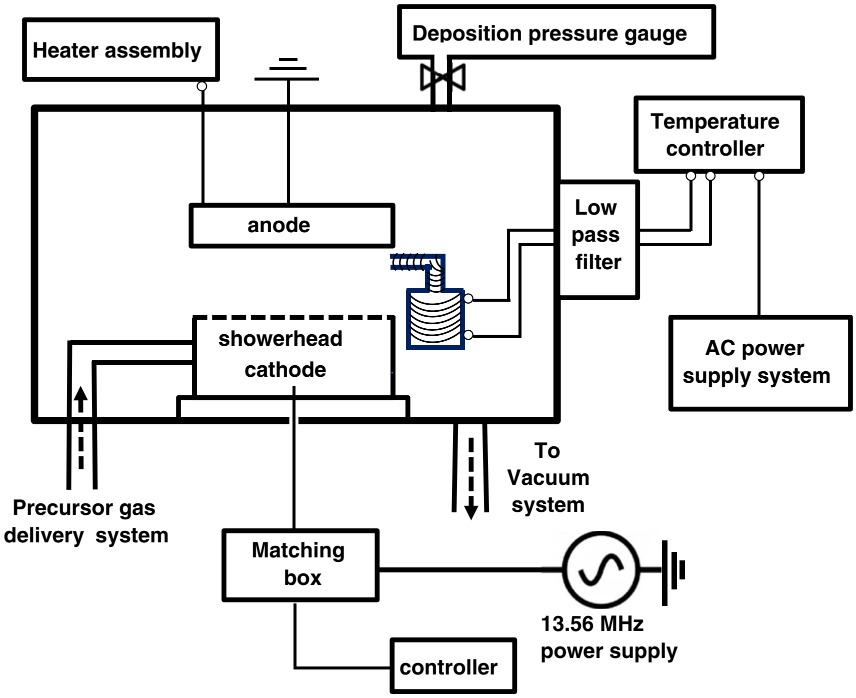

Fig. 1. Schematic diagram of the MO-RFPECVD system used for the preparation of a-C:H(Er) films.