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Fundamentals of $Ge_{1-x}Sn_x$ and $Si_yGe_{1-x-y}Sn_x$ RPCVD epitaxy

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ABSTRACT

We have studied epitaxial growth of $Ge_{1-x}Sn_x$ and $Si_yGe_{1-x-y}Sn_x$ materials in 200 mm and 300 mm industrial CVD reactors using industry standard precursors. The growth kinetics of undoped GeSn were firstly studied via varying growth parameters including growth temperatures, $GeH_4$and $SnCl_4$precursor flows, which indicated that the material growth is highly dependent on surface kinetic limitations involving the $SnCl_4$reaction pathway. Secondly, the growth kinetics of doped layer growth by varying the growth temperatures and the $PH_3$and B_2H_6dopants flows were investigated. It was shown that B_2H_6had the effect of increasing the growth rate and decreasing the Sn incorporation whereas PH_3had no effect on the growth rate but increased the Sn incorporation. Thirdly, the SiGeSn growth kinetics using SiH_4, GeH_4, and $SnCl_4$as precursors were discussed, which revealed that the careful control of the growth rate was required to produce compositionally homogenous SiGeSn alloy. Moreover, the material and optical characterizations have been conducted to examine the material quality. Finally, the GeSn quantum well structure was grown to exhibit the precise control of the growth parameters.

1. Introduction

$Ge_{1-x}Sn_x$ and $Si_yGe_{1-x-y}Sn_x$ materials offer promising technical advantages compared to traditional group IV semiconductors. The incorporation of Sn into SiGe and Ge enables novel strain engineering in advanced complementary metal oxide semiconductors (CMOS) devices due to the tunable lattice constant [1,2]. The alloy also has a tunable band-gap which transitions to direct bandgap material at Sn compositions greater than ~8% making it great potential for optoelectronic applications [3–7]. However, (Si)GeSn materials have not yet been adopted in any commercialized semiconductor device applications mainly due to the lack of mature material growth techniques. Epitaxial growth of device quality alloys is still difficult for a number of reasons such as high dislocation density, Sn-segregation/precipitation, and amorphous inclusions. Over the past a few years several research groups have demonstrated high-quality layers using various growth methods [8–12], however all-to-often highly specialized growth approaches are required which are not compatible with semiconductor manufacturing methods. The reported resultant processes have low throughput (using molecular beam epitaxy, MBE or ultra-high vacuum chemical vapor deposition, UHV-CVD) and/or require expensive, non-standard precursors (Ge_2H_6 and SnD_4). In order for the material to meet widespread use in consumer devices high-quality, cost-effective, repeatable epitaxial growth must be established on industry standard depositions tools utilizing standard precursors such as GeH_4 and SiH_4. $SnCl_4$ as Sn precursor does not currently see widespread use in semiconductor manufacturing however it is considered to be more suitable than SnD_4 which requires very specialized preparation, handling, and storage.

A preliminary study of the growth of $Ge_{1-x}Sn_x$ using GeH_4 and $SnCl_4$ on an industrial RPCVD tool have been reported [12]. In this work we present a more detailed study of the GeSn growth mechanism and growth kinetics on the ASM Epsilon® 2000 (200 mm) as well as on the 300 mm ASM Intrepid XP™ with GeH_4 and $SnCl_4$. The in-depth investigation of growth process is conducted. Material and optical characterization are conducted to further examine the material quality. Based on our understanding of the growth fundamentals, we demonstrate a GeSn quantum well (QW) structure with precise interfacial

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control. This shows the feasibility of GeSn and SiGeSn device architectures in large-scale semiconductor manufacturing.

2. Experimental method

Epitaxial $Ge_{1-x}Sn_x$ and $Si_yGe_{1-x-y}Sn_x$ layers were grown on ~ 0.7 µm Ge-buffered Si substrate (100) using the ASM Epsilon® 2000 and the ASM Intrepid XPTM systems. The ASM Epsilon® reactor is a load-locked, horizontal flow, 200 mm single wafer reduced-pressure CVD (RPCVD) system which is designed for high-volume semiconductor manufacturing (HVM) for diverse epitaxy applications. The Intrepid XP™ is a 300 mm single wafer RPCVD system designed specifically to meet the demands of advanced CMOS and memory epitaxy applications. In both of these systems the wafer sits on a SiC coated graphite susceptor in a cold wall quartz chamber. Two lamp arrays positioned on the top and bottom of the quartz chamber heat the reactor during processing. Low-temperature GeSn growth is controlled by thermocouples which are embedded in the susceptor.

Germanium buffer layers (approximately 700 nm thick) were grown in-situ prior to GeSn growth using 10% GeH_4 in purified H_2 carrier gas. Prior to growth of the Ge buffer layer the silicon substrate is heated to 1060 °C at 20 Torr to remove the native oxide. The buffer layers were grown by a two-step growth method. First, a 150 nm seed layer was grown at < 400 °C in H_2 carrier at a GeH_4 partial pressure of 0.2 Torr, then the temperature was increased to 600 °C. Once the temperature has stabilized at 600 °C, the remaining ~ 500 nm was grown and a post-growth in-situ anneal was done at > 800 °C. The chamber was then cooled down to < 400 °C in H_2 and then the GeH_4, (SiH_4) and $SnCl_4$ precursors were introduced into the chamber to initiate the (Si) GeSn film growth. $SnCl_4$ is a liquid at room temperature and must be delivered using a bubbler held at room temperature in which H_2 gas is metered to it to increase or decrease to the desired $SnCl_4$ mass flow rate. The $SnCl_4$ mass flow rate was measured up-stream of the bubbler by a piezoelectric acoustic sensor. This signal was fed back to H_2 bubbler mass flow controller (MFC) in a dynamic control loop to continually monitor and adjust the $SnCl_4$ relative to the desired set-point. In this work we report the $SnCl_4$ flow rate as the molar flow fraction, $M_{SnCl4} = m_{SnCl4}/(m_{GeH4} + m_{H2} + m_{SnCl4})$), where m_x denotes the respective molar flow rate for each precursor. For the doped GeSn growth, the 1% PH_3 and 1% B_2H_6 in H_2 were used for growth of n- and p-type layers, respectively.

The thicknesses and compositions of the grown layers were measured by X-ray diffraction (XRD) and secondary-ion mass spectrometry (SIMS). The ω−2θ coupled scans on the (004) reflection were done using the Phillips X′pert Pro X-ray diffractometer. The SIMS analysis was done using an Atomika 4500 with Cs^+ ion source and beam energies ranging from 0.5 to 5 keV depending on the desired depth resolution. Cross-sectional transmission electron microscopy (TEM) was used for characterize the layer defectivity.

The photoluminescence (PL) was conducted to study material quality and the band structure. The PL measurements were performed using a standard off-axis configuration with a lock-in technique (optically chopped at 40 Hz). A continuous wave (CW) laser with 532 nm wavelength was used as an excitation source. The laser beam was focused down to a 100 µm spot and the power was measured to be 400 mW. The PL emission was collected by a spectrometer and then sent to a PbS detector with a cut-off at 3.0 µm.

3. Results and discussions

3.1. Growth fundamentals and mechanism study via undoped GeSn growth

The understanding of the initial stages of heteroepitaxial growth is very important, through which the defect generation and relaxation can be better controlled. The early stages of growth are usually delayed by the formation of islands which then coalesce to form a continuous layer. Based on our experience a nucleation delay time (t_0) for the growth of GeSn can be up to 80 s Fig. 1 plots the GeSn layer thicknesses as functions of growth time with Sn compositions of 3% and 7%. An identical growth rate of 22 nm/min was observed, indicating the delay time to be independent of growth rate. The nucleation delay times of 79 and 56 s were extracted for 3% and 7% Sn layers, respectively. The growth modes are described by Bauer [13] as a balance between interfacial energy and strain energy. The Sn atom has a lower surface energy than the Ge atom so that an alloy of GeSn should wet a Ge surface from a surface energetics point-of-view. Obviously the addition of Sn to the Ge lattice should also introduce interfacial strain energy which can counteract the layer wetting and 2-dimensional growth. Under certain conditions these considerations can lead to an epitaxial nucleation delay. However those considerations are most valid when growth conditions are close to thermodynamic equilibrium and CVD growth of GeSn is far from equilibrium. The delay is most likely representative of a kinetic limitation. In Fig. 1 the growth condition of 7% Sn layer was with a higher M_{SnCl4} (molar flow ratio) than that of the 3% Sn layer. Therefore this may be indicative that the kinetic pathway $SnCl_4$ (g) → Sn*→ Sn-Ge is responsible for the nucleation delay.

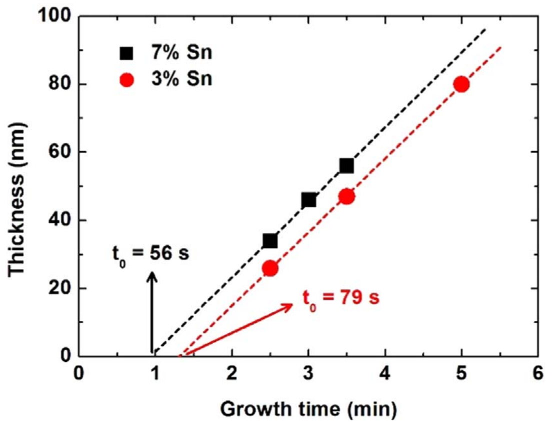

Fig. 1. GeSn layer thicknesses vs. growth time for 3% and 7% Sn layers. The growth rates for both conditions were 22 nm/min. The nucleation delay times (t_0) of 79 and 56 s were extracted for 3% and 7% Sn layers, respectively.

The CVD growth mechanism of GeSn has not been well understood thus far. Generally speaking, the reaction proceeds by the dissociative adsorption and reaction of $SnCl_4$ and GeH_4 molecules on the growth surface to form $SnCl_x$ and GeH_y along with H* and Cl* adatoms. The presence of these adatoms implies the formation of a variety of surface species e.g. Ge-Cl, Ge-H, Sn-Cl, Sn-H, etc. Subsequent surface reactions such as the reduction of $SnCl_x$ by GeH_y can lead to the direct formation of crystalline GeSn. Other possible reactions could include the reduction of Sn-Cl and/or Ge-Cl by surface H and subsequent formation of mobile Sn* and Ge* adatoms which could diffuse across the growth terrace and incorporate at ledge/kink sites. The presence of Cl on surface also induces etching along with deposition [14,15]. Therefore, in order to achieve GeSn growth the etching rate from the surface Cl has to be less than the deposition rate of the film.

Fig. 2(a) shows the growth rate as a function of $SnCl_4$ molar flow fraction (M_{SnCl4}). In comparison to the growth of Ge using GeH_4 (M_{SnCl4} =0), the addition of $SnCl_4$ to the chemistry results in an initial drop in growth rate due to etching process. The increase in growth rate was observed for $M_{SnCl4} > 1.7\times10^{-5}$. This is due to the catalytic effect of increased Sn fraction on the surface which enhances the surface H and Cl desorption rates due to the lower Sn-H(Cl) bond energy relative to Ge-H(Cl) [16].

Experimental data suggest that the GeH_4 molecule is required for the reduction on $SnCl_4$ and the subsequent incorporation of Sn into the epitaxy layer. Fig. 2(b) shows the Sn incorporations as functions of