# High-quality Ge and Sn Thin Films Deposited on Si Substrate by Magnetron Sputtering

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**Abstract:**  $Ge_x Sn_{1-x}$  is one of the most promising materials in optoelectronics for its direct band-gap nature. In this paper, we report high-quality Ge and Sn thin films deposited on Si (001) substrates by magnetron sputtering. We found that the growth power and chamber pressure affect the quality of the Ge and Sn thin films significantly but in different ways. By optimizing the deposition conditions, high quality Ge and Sn films are achieved. A clear peak of Ge (004) phase in the x-ray diffraction (XRD) pattern which indicates a high-quality Ge lattice formed is observed, and post-treatment like rapid thermal annealing does not significantly affect the quality of the thin films.

Keywords: GeSn; thin film; magnetron sputtering

## 1. INTRODUCTION.

Group IV semiconductors such as silicon (Si) and germanium (Ge) have proven their advantages in the mass production of electronic devices in the past decades. As for optoelectronic devices, group IV semiconductors have serious limitations because of their indirect band-gap structure. Instead, direct band-gap III-V compounds are mostly employed in optoelectronic applications [1-7]. Since the main obstacle for group IV materials to realize optoelectronic properties is the very close energy difference between its direct gap and indirect gap, band gap engineering by inducing lattice strain or alloying becomes a promising method. Silicon is a very large band-gap material. As its difference between the direct and indirect band gaps is significant (2.54 eV), it is almost impossible for Silicon to tune the nature of band gap from indirect to direct. While for Germanium, the difference between the direct ( $\Gamma$  valley) and indirect (L valley) gaps is only 0.14e V, also known as a pseudo-direct band-gap material, hence it is a very interesting material for applications in optoelectronic devices [8, 9, 10].

Researchers keep trying to find direct band-gap materials that can grow on silicon substrates to replace the expensive III-V materials [11, 12, 13]. Recently, S. Wirths at el. have reported observing lasing effect in the direct band-gap bulk GeSn fabricated by a chemical vapor deposition (CVD) method. They overcame the lattice mismatch issue by introducing a virtual buffer layer between the bulk GeSn and substrate [14].

In this work, we report high-quality Ge and Sn thin films fabricated a using magnetron sputtering method, which is the pre-work for deposit GeSn alloys. The morphology such as surface roughness and surface nano particles is characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Our results show that these two materials react differently to the growth conditions. The quality of the Ge thin film which in our case is very sensitive to the chamber pressure while the quality of Sn thin films is more sensitive to growth power. The single crystalline structure is confirmed by the HR-XRD in which a sharp peak with a full width half maximum of around 0.3 degree is observed.

### 2. EXPERIMENTAL SET-UP.

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The Ge and Sn targets are separately set on a radio frequency (RF) source and a direct current (DC) source, respectively [15]. At beginning, the Si (001) substrate is treated by chemicals for a clean surface. It is first immersed into acetone solution in ultrasonic cleaner for 3 minutes in order to wipe out organic substance such as grease, paint and glue. Then isopropyl alcohol is used for further cleaning. Its volatility guarantees this is no residual remaining on the substrate surface.

Before the sputtering process starts, the chamber is pumped to high level vacuum at around  $8 \times 10^{-6}$  mTorr to eliminate particles and other polluting gases which may affect the quality of the thin film. The growth time is fixed at 1800 seconds to reach an enough thickness for a uniform profile. The substrate is rotated at a rate of one round every two seconds during sputtering in order to get a more uniform film and to cancel out some random mechanism which is produced by the tool itself. Argon is chosen for the ion source [16, 17].

The chamber pressure and power in the sputtering process are the main factors that will affect the quality of the films. The chamber pressure mainly affects the density of the Argon ions in the chamber, while the power influences the strength of electric field which will accelerate the ionized Argon atoms to travel to wards negatively biased target [18,19].

### 3. RESULTS AND DISCUSSIONS.

The roughness data of Ge thin films are obtained by inspecting the surface profile through AFM and SEM as shown in Figure 1 and 2, respectively. The growth power and the chamber pressure for the 4 samples are 40 W and 5 mTorr for sample 1 (S1); 40 W and 10 mTorr for S2; 80 W and 5 mTorr for S3; 80 W and 10 mTorr for S4.

As we can see, the roughness of the surface is very sensitive to the chamber pressure. The chamber pressure directly determines the density and the size of the nano bumps observed through AFM on the thin film surface. A low value of chamber pressure is suitable for a smooth surface of the Ge films. It is likely that under low pressure, there is less atom collision occurred so that the target atoms can go straight towards the substrate more likely once they are dislodged from target. This can provide a higher uniformity of the atoms ' energy reaching the substrate rather than transferring energy with each other during collision. As for growth power, it merely affects the growth rate. The changing power slightly influences the roughness of surface or the size of the particle on the surface that is displayed in Figure 2.



Fig. 1. AFM images of the Ge thin films deposited at different pressure and powers.



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Fig. 2. SEM images of the Ge thin films deposited under different pressures and powers.

Similar characterization is also carried out for the Sn thin films. The growth power and the chamber pressure for the 4 samples are: 5 W and 5 mTorr for S5; 5 W and 10 mTorr for S6; 10 W and 5 mTorr for S7; 10 W and 10 mTorr for S8. The results are demonstrated in Figure 3 and 4, respectively. It is found that the morphology behavior of the Sn thin films is quite different from that of Ge thin films. For Sn thin film deposition, the roughness of surface is now more sensitive to the power rather than chamber pressure comparing to Ge deposition. This is due to its intrinsic physical properties of Sn as it is a malleable and ductile conductor material. When Argon ions with high energy are bombarding on the Sn target under a large power, instead of single atom or small clusters of atoms, large clusters that contain many of Sn atoms will easily deposit on the substrate. This is verified through SEM images where the size of the clusters is significantly increased when a large power is used. In this case, even the chamber pressure changes the roughness, the change is not as significant as the growth power [20].



Fig. 3. AFM images of the Sn thin films deposited under different pressures and powers.



Fig. 4. SEM images of the Ge thin films deposited under different pressures and powers.

The relation between the average roughness and the growth condition is displayed in Figure 5. For Ge thin films, increasing both chamber pressure and the target power will enlarge the roughness. According to our experiments, the growth power to 60 watt and minimum chamber pressure are the best conditions for smooth Ge films. For Sn thin films, the chamber pressure does not significantly influence the roughness. It is only sensitive to the power, especially at a power of 5 W.



Fig. 5. Average roughness as the function of chamber pressure for (a) Ge deposition; (b) Sn deposition.

Deposition rate is estimated by surface profiler on a step structure formed by a hard mask. The deposition rates for both materials are closely related to the power and chamber pressure. It is found that with the chamber pressure fixed, the deposition rate for both materials increases monotonically. When the power is fixed, however, the deposition rate will increase first quickly with the increasing chamber pressure, then slowly and finally saturate. This is because the Argon ion density in which can bombard the target reaches its upper limitation due at a fixed power.



Fig. 6. The deposition rate as a function of (a) power for Ge; (b) chamber pressure for Ge; (c) power for Sn; (d) chamber pressure for Sn.

We also studied the crystallography of the Ge thin films because it is the main concern for forming high-quality GeSn alloy. We used HR-XRD to analyze the  $\Box \Box 2\Box$  relation of the samples under different thermal treatments. The XRD results is shown in Figure 7 in logarithm scale. The (004) phase of Ge is clearly observed in the graph. The strength of the signal is 10k times smaller comparing to the single crystalline Si (001) substrate that is acceptable. The full width half maximum (FWHM) is less than 0.3 degree which refers to quite a good quality that is obtained in this sample. The rapid thermal treatment from 500 towards 700 degree for 90 seconds leaves almost n o influence on the crystal quality.



Fig. 7.  $\Omega$ -20 relation of Ge on Si with different thermal treatments.

# 4. CONCLUSION.

Instead of CVD and MBE which are commonly used for growing single crystalline Ge and Sn thin films, we used magnetron sputtering to prepare high-quality Ge and Sn thin films at room temperature. Our results show that these two materials react differently to the growth conditions. The quality of the Ge thin film is very sensitive to the chamber pressure while the quality of Sn thin films is more sensitive to growth power. The single crystalline structure of Ge is confirmed by the HR-XRD in which a sharp peak with a full width half maximum of around 0.3 degree is observed, and the peak shape and line width do not change significantly by an nealing.

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