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Orientation epitaxy of $\text{Ge}_{1-x}\text{Sn}_x$ films grown on single crystal CaF_2 substrates

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Abstract

$\text{Ge}_{1-x}\text{Sn}_x$ films were grown via physical vapor deposition below the crystallization temperature of Ge on single crystal (111) and (100) CaF_2 substrates to assess the role of Sn alloying in Ge crystallization. By studying samples grown at several growth temperatures ranging from 250 °C to 400 °C we report temperature-dependent trends in several of the films' properties. X-ray diffraction theta vs. two-theta ($\theta/2\theta$) scans indicate single orientation $\text{Ge}_{1-x}\text{Sn}_x(111)$ films are grown on $\text{CaF}_2(111)$ substrates at each temperature, while a temperature-dependent superposition of (111) and (100) orientations are exhibited in films grown on $\text{CaF}_2(100)$ above 250 °C. This is the first report of (111) oriented $\text{Ge}_{1-x}\text{Sn}_x$ grown on a (100) oriented CaF_2 substrate, which is successfully predicted by a superlattice area matching model. These results are confirmed by X-ray diffraction pole figure analysis. $\theta/2\theta$ results indicate substitutional Sn alloying in each film of about 5%, corroborated by energy dispersive spectroscopy. Additionally, morphological and electrical properties are measured by scanning electron microscopy, atomic force microscopy and Hall mobility measurements and are also shown to be dependent upon growth temperature.

Introduction

Semiconductor films exhibiting high mobilities and adjustable bandgaps can be used in silicon based optoelectronics and have been researched in the past several decades^{1,2}. Numerous studies have been conducted which have demonstrated the potential of $\text{Ge}_{1-x}\text{Sn}_x$ alloy for implementation in near-IR photodetectors and photodiodes^{3,4} and lasers⁵⁻⁷. $\text{Ge}_{1-x}\text{Sn}_x$ alloyed film is an attractive option because at low concentrations of Sn, the alloy undergoes an indirect to direct bandgap transition, which can be adjusted by altering Sn concentration. In addition, Sn has been shown to serve as a surfactant, lowering the temperature needed for Ge crystallization by increasing the diffusion of Ge adatoms, thus the energy costs of producing Ge films can be reduced by alloying with Sn⁸. This is done at no cost to the films' electrical properties because Sn and Ge are in the same chemical group. As a result, $\text{Ge}_{1-x}\text{Sn}_x$ films have demonstrated potential for application in cost-effective optoelectronics. Although the atomic size of Sn is ~15% larger than that of Ge, Sn atoms substitute in place of Ge atoms in Ge lattice sites⁹⁻¹¹. Therefore, the lattice constant of $\text{Ge}_{1-x}\text{Sn}_x$ increases from that of pure Ge ($a_{\text{Ge}} = 0.5658$ nm) depending on the relative amount of Sn. The crystal symmetry of $\text{Ge}_{1-x}\text{Sn}_x$, however does not change from that of pure Ge. Our recent work demonstrated that ~600 nm thick $\text{Ge}_{1-x}\text{Sn}_x(111)$

film having a biaxial texture can be grown at temperatures below the crystallization temperature of pure Ge (of over 400 °C) on an amorphous (glass) substrate using an array of biaxial $\text{CaF}_2(111)$ nanorods capped with a $\text{CaF}_2(111)$ buffer layer⁸. The out-of-plane and in-plane dispersions in the textured $\text{Ge}_{1-x}\text{Sn}_x(111)$ film were $10.8 \pm 0.2^\circ$ and $14.2 \pm 0.7^\circ$ degrees, respectively. These dispersions originate from the dispersions in the biaxial CaF_2 substrate^{12, 13}.

In this work we report the results of $\text{Ge}_{1-x}\text{Sn}_x$ alloy films grown on single crystal $\text{CaF}_2(111)$ and (100) substrates at several temperatures below the crystallization temperature of pure Ge, ranging from 250 °C to 400 °C in 50 °C increments. Each set of films was deposited simultaneously on both $\text{CaF}_2(111)$ and (100) substrates to ensure identical growth conditions. First, we note that the texture quality of the $\text{Ge}_{1-x}\text{Sn}_x$ films grown on single crystal $\text{CaF}_2(111)$ greatly improves from that of the $\text{Ge}_{1-x}\text{Sn}_x$ film grown on biaxial $\text{CaF}_2(111)$ on glass and is independent of temperature within the studied range. The out-of-plane direction is [111] and the in-plane epitaxy relationships are $\langle 1\bar{2}1 \rangle_{\text{Film}} \parallel \langle 1\bar{2}1 \rangle_{\text{CaF}_2}$ and $\langle \bar{1}01 \rangle_{\text{Film}} \parallel \langle \bar{1}01 \rangle_{\text{CaF}_2}$. Second, in the films grown on $\text{CaF}_2(100)$ we observe an out-of-plane orientation that changes with temperature. The film grown at 250 °C exhibits a single-orientation [100] growth direction, while those grown at each higher temperature exhibit a combination of (100) and (111) orientations. The data herein is the first report of the latter. In addition, this serves as the first study of $\text{Ge}_{1-x}\text{Sn}_x$ alloy films grown on $\text{CaF}_2(100)$ substrates, which provides comparison to those grown on $\text{CaF}_2(111)$ substrates. The corresponding in-plane epitaxial relationships are: $\langle 010 \rangle_{\text{Film}} \parallel \langle 010 \rangle_{\text{CaF}_2}$ and $\langle 001 \rangle_{\text{Film}} \parallel \langle 001 \rangle_{\text{CaF}_2}$ for the (100) orientation and are $\langle 1\bar{2}1 \rangle_{\text{Film}} \parallel \langle 011 \rangle_{\text{CaF}_2}$ and $\langle \bar{1}01 \rangle_{\text{Film}} \parallel \langle 01\bar{1} \rangle_{\text{CaF}_2}$ for the (111) orientation.

The structure and texture of films were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD) including theta vs. two-theta ($\theta/2\theta$) scans, rocking curves (RCs) and pole figure analysis. Morphology of films was examined by scanning electron microscopy (SEM) as well as atomic force microscopy (AFM), with roughness parameters quantified by height-height correlation analysis¹⁴. Energy dispersive spectroscopy (EDS) and Hall mobility measurements were used to investigate chemical composition, homogeneity, and electrical properties of films. Films' electrical properties are shown to depend on growth temperature and differ slightly from those of $\text{Ge}_{1-x}\text{Sn}_x$ films grown by other methods as well as pure Ge films.

Experimental

Samples were grown via normal incidence physical vapor deposition onto single crystal $\text{CaF}_2(111)$ and (100) substrates (MTI Corp., 10 mm × 10 mm × 1 mm). The out-of-plane direction of each starting substrate was within $\pm 1.5^\circ$ of that which was specified. Depositions were administered in a vacuum chamber pumped down to a base pressure on the order of 10^{-8} Torr. Alumina-coated W baskets containing the deposition materials (Ge, 99.9% pure; Sn, 99.99% pure; Kurt J. Lesker Co.) were placed approximately 30 cm below the substrate and heated via electrical current to achieve evaporation at the desired flux rate in the range of $1.5 - 2.5 \text{ Ås}^{-1}$. Deposition rate and thickness were monitored by a quartz crystal microbalance and calibrated from cross-sectional TEM and SEM images. Figure 1 outlines the growth procedure. For each sample, 35 nm of Sn was deposited without intentional substrate heating, followed by 500 nm of Ge deposited with the substrate heated to 250 °C, 300 °C, 350 °C, or 400 °C, with uncertainties of approximately $\pm 5^\circ\text{C}$. The time between Sn and Ge depositions was

approximately 45 minutes. Samples were subsequently annealed at the Ge deposition temperature *in situ* for one hour. This has previously been shown to enhance the crystallization of $\text{Ge}_{1-x}\text{Sn}_x$ films.

A Zeiss Supra 55 SEM was used to acquire electron micrographs as well as EDS spectra of samples using a beam energy of 2 keV with a 30 μm aperture and a beam energy of 10 keV with a 60 μm aperture for imaging and compositional measurements, respectively. The transmission electron microscopy (TEM) sample was prepared by *in-situ* focused ion beam (FIB) lift out. Conducting layers of Au and Pt were deposited on the film surface for cross-sectioning with energetic Ga ions. A JEOL 2100F TEM was used to collect cross-section bright-field images, high resolution images, and diffraction patterns (200 kV). A Hitachi 2700C TEM was used to collect EDS spectra (200 kV) throughout the thickness profile and for compositional mapping. 8 $\mu\text{m} \times 8 \mu\text{m}$ AFM images were taken using a Park Systems XE7 Scanning Probe Microscope in non-contact mode at a selected frequency in the range of 322 - 328 kHz, using a cantilever with a spring constant of approximately 42 Nm^{-1} . XRD scans were obtained using a Bruker D8 Discover X-ray diffractometer ($\text{Cu K}\alpha$, $\lambda = 1.5405 \text{ \AA}$) with a point detector. The incident beam, detector, and anti-scatter slits used to achieve maximum resolution were 0.1 mm, 0.1 mm and 0.2 mm, respectively. X-ray pole figures were collected using larger slits, each of width 0.6 mm, to maximize signal. Peak parameters were extracted from Gaussian fits obtained using ORIGIN software. Hall mobility measurements were made using a current of 1 mA and under a magnetic field of 0.45 Tesla. To create electrical contacts, Indium was secured to the surface of each film at room temperature (and without annealing) by applying pressure.

Results and Discussion

A. Morphology evolution of $\text{Ge}_{1-x}\text{Sn}_x$ films on single crystal CaF_2

SEM images and AFM scans were taken to observe as well as quantify the films' temperature-dependent evolution in morphology. These are shown in Fig. 2 for films grown at 250, 300, 350, and 400 $^\circ\text{C}$. The films' morphologies are dramatically different from the smooth surfaces of the starting substrates (each CaF_2 substrate has an RMS roughness less than 1 nm). The surfaces of samples grown at 300 $^\circ\text{C}$ appear the smoothest in the vertical direction. Samples grown at 250 $^\circ\text{C}$ contain many small spherical clusters with diameters of a couple hundred nanometers. These features grow laterally with increasing growth temperature. At the higher growth temperatures of 350 $^\circ\text{C}$ and 400 $^\circ\text{C}$ the films' surfaces contain larger clusters on the order of one micron in diameter. The spherical features observed on the surface of each film results from surface energy differences between the substrates and films. The energies of the (111) and (100) surfaces of Ge (1.06 Jm^{-2} and 1.84 Jm^{-2})¹⁵ and Sn (1.03 Jm^{-2} and 0.80 Jm^{-2})¹⁶ differ from those of CaF_2 (0.45 Jm^{-2} and 0.98 Jm^{-2})^{17, 18}. Thus we expect the growth of $\text{Ge}_{1-x}\text{Sn}_x$ on CaF_2 in the form of Volmer-Weber (VW) islands. The formation of 3D $\text{Ge}_{1-x}\text{Sn}_x$ VW islands has been observed on various substrates^{19, 20} including biaxial $\text{CaF}_2(111)$ nanorods⁸.

For a more in-depth comparison of the films' morphologies, 8 μm by 8 μm AFM images were used to calculate several roughness parameters. We analyzed the two-dimensional height-height correlation function, $H(\mathbf{r})$ to extract vertical surface width (or RMS roughness in the surface normal direction), ω , lateral correlation length, ξ , and roughness exponent, α ¹⁴. $H(\mathbf{r})$ is defined as $H(\mathbf{r}) = \langle [h(\mathbf{r}) - h(0)]^2 \rangle$, where $h(\mathbf{r})$ is the surface height at position $\mathbf{r}$ and $h(0)$ is the surface

height at a reference position $\mathbf{r} = 0$. The surface width, ω is the square root of $\langle [h(\mathbf{r}) - \langle h \rangle]^2 \rangle$, which describes the surface roughness at large distances. $\langle h \rangle$ is the average height at the surface. The lateral correlation length, ξ describes the “wavelength” of the surface fluctuations. For large r , the surface height fluctuations should not be correlated, so $H(r) = 2\omega^2$. For small r , the surface height-height correlation has the asymptotic form $H(r) = (\rho r)^{2\alpha}$, where ρ is a constant and α is the local roughness exponent. α describes how “wiggly” the surface is and has a value ≤ 1 , with 1 being the smoothest and decreasing values corresponding to locally rougher surfaces. Table 1 lists the extracted numbers.

Table 1. Roughness parameters of $\text{Ge}_{1-x}\text{Sn}_x$ films determined by height-height correlation analysis of AFM images.

Film	Growth Temp. (°C)	ω (nm)	ξ (nm)	α
$\text{Ge}_{1-x}\text{Sn}_x$ / $\text{CaF}_2(111)$	250	49.1	112	0.72
	300	34.6	160	0.80
	350	50.3	225	0.76
	400	97.2	356	0.73
$\text{Ge}_{1-x}\text{Sn}_x$ / $\text{CaF}_2(100)$	250	56.9	159	0.74
	300	35.0	165	0.68
	350	69.1	296	0.77
	400	121.2	410	0.75

In agreement qualitatively with SEM and AFM images in Fig. 2, lateral correlation length increases with growth temperature, indicating larger lateral dimensions of surface features. This is consistent with previous temperature-dependent work on $\text{Ge}_{1-x}\text{Sn}_x$ alloy films grown on biaxial $\text{CaF}_2(111)$ nanorods⁸. RMS roughness follows a trend similar to lateral correlation length. It increases with growth temperature above 300 °C, but is $\sim 40 - 60\%$ lower for films grown at 300 °C than for those grown at 250 °C. At each growth temperature, samples grown on $\text{CaF}_2(100)$ have larger features than are exhibited on the surfaces of films grown on $\text{CaF}_2(111)$. Roughness exponent is independent of both growth temperature and substrate orientation.

Fig. 3(a) shows a TEM bright-field image taken of the cross-section of the substrate/film interface of the $\text{Ge}_{1-x}\text{Sn}_x$ film grown on $\text{CaF}_2(111)$ at 400 °C. An ultrathin conducting Au layer and protective Pt layer were deposited on the film surface before FIB milling. The film thickness varies between approximately 300 and 450 nm (the scale bar indicates 200 nm).

B. Chemical composition of $\text{Ge}_{1-x}\text{Sn}_x$ films on single crystal CaF_2

EDS spectra were collected at ten locations throughout each sample surface to analyze the films’ chemical compositions. Due to the $\sim 1 \mu\text{m}$ penetration depth of the 10 kV electron beam used, signals of Ca and F were detected from the substrate in addition to the Ge and Sn in the film. Trace amounts of C, H, and O were also detected, presumably from contamination during the post-deposition handling of the films out of vacuum. By discounting the signals due to the substrate and impurities, we estimate the percentage of Sn alloying in each sample, listed in Table 2.

Table 2. Sn alloying percentages (x) determined by EDS. Data were collected from ten regions of each sample. Errors indicate one standard deviation in the data.

Film	Growth Temp. (°C)	x (%)
Ge_{1-x}Sn_x / CaF₂(111)	250	4.52 ± 0.28
	300	5.54 ± 0.59
	350	6.01 ± 0.45
	400	6.04 ± 0.46
Ge_{1-x}Sn_x / CaF₂(100)	250	5.46 ± 0.33
	300	5.41 ± 0.45
	350	6.23 ± 0.51
	400	6.39 ± 0.41

Each sample is determined to be between approximately 4.5% and 6.4% Sn with standard deviations of about 0.5%. The data show a slight tendency toward higher levels of Sn alloying at higher growth temperatures, although with the relatively large errors of up to 10% inherent in this type of analysis, no definite conclusions can be made.

In addition, EDS spectra were collected across the thickness profile of the film grown on CaF₂(111) at 400 °C (shown in Fig. 3(a)) to assess the film's homogeneity. The results are shown in Fig. 3(b). The Sn composition varies between 2% and 8% with an average of approximately 2.9%, slightly lower than indicated by normal incidence EDS. Comment on difference? The inset in Fig. 3(b) is a spatial map of the alloy composition, which is used to qualitatively assess the homogeneity of the film. Green and red data show signal from Ge and Sn, respectively, while black regions indicate areas from which no data were collected. Sn content appears uniformly distributed throughout the film, indicating homogeneous incorporation of Sn atoms within the Ge lattice.

The 35 nm Sn layers in these samples are less than half as thick as the 75 nm layer that was needed to achieve similar levels of Sn alloying in Ge_{1-x}Sn_x on biaxial CaF₂(111) nanorods⁸. We attribute this to the better uniformity of the single crystal CaF₂ substrates as compared to the biaxial CaF₂ substrates, into which some of the pre-deposited Sn was able to diffuse into gaps between nanorods. The smoother surface of single crystal CaF₂ allows for more efficient incorporation of Sn into the film layer.

C. Out-of-plane texture evolution of Ge_{1-x}Sn_x films on single crystal CaF₂

As described in previous sections, compared to those of the CaF₂ substrates, the surfaces of the Ge_{1-x}Sn_x films exhibit dramatically different morphological features. Morphologies were also observed to change with growth temperature. The crystallinity of films may differ not only from that of the substrates, but may also evolve with growth temperature. X-ray theta vs. two-theta ($\theta/2\theta$) scans of each film were run to investigate this possibility.

The Bragg peak position obtained from a $\theta/2\theta$ scan provides information about the lattice constant and out-of-plane orientation of a film. The FWHM of a Bragg peak intensity profile after deconvolution with the appropriate instrument response function is approximately inversely proportional to the average size of the ordered regions in the direction perpendicular to the substrate, or in the direction parallel to the momentum transfer vector ($\mathbf{S}$ = outgoing wavevector

$\mathbf{k}_{\text{out}}$ minus incident wavevector $\mathbf{k}_{\text{in}}$)²¹. $\theta/2\theta$ scans were run for each sample and revealed peaks due to each film in addition to each substrate. (111) oriented CaF_2 substrates exhibited (111) and (222) peaks while each (100) oriented CaF_2 substrate exhibited (200) and (400) peaks. For brevity substrate peaks are not shown. From the location of each peak, we use Bragg's law to determine the lattice constant of each substrate to be 0.5463 nm, close to the bulk CaF_2 lattice constant of 0.5462 nm. Film peaks of samples grown on each substrate at each temperature are shown in Fig. 4 with the data extracted from Gaussian fits using ORIGIN software compiled in Tables 3 and 4 for samples grown on $\text{CaF}_2(111)$ and $\text{CaF}_2(100)$, respectively (Full range $\theta/2\theta$ scans for each film are included in Supplementary Information Figs. S1 and S2). The FWHMs of the single-crystal substrate peaks were used as the instrument response functions for deconvolution of the corresponding film peaks. Listed FWHM values have been deconvoluted with those of the corresponding substrate peaks ($0.027^\circ - 0.031^\circ$ for $\text{CaF}_2(111)$, $0.028^\circ - 0.033^\circ$ for $\text{CaF}_2(200)$ and $0.038^\circ - 0.044^\circ$ for $\text{CaF}_2(400)$).

Fig. 3(c) shows a high-resolution TEM image of a defect-free region in the $\text{Ge}_{1-x}\text{Sn}_x$ film grown on $\text{CaF}_2(111)$ at 400°C . d_{111} is indicated on the image and was measured to be $3.27 \pm 0.05 \text{ \AA}$, in good agreement with the theoretical value of $3.29 \text{ \AA}$. A selected area diffraction pattern is included in the inset. The symmetry of the diffraction spots indicates a $[011]$ zone axis. Reciprocal lattice vectors g_{111} and g_{200} are shown as solid arrows emanating from the 000 spot. Their distances were measured to be approximately 2.96 nm^{-1} and 3.37 nm^{-1} , giving real space values for d_{111} and d_{200} of $3.38 \text{ \AA}$ and $2.97 \text{ \AA}$, respectively. These, too, are consistent with d_{111} and d_{200} using the lattice constant $5.70 \text{ \AA}$ determined from XRD, shown in the fifth row of Table 3, and theoretical values ($d_{111} = 3.29 \text{ \AA}$ and $d_{200} = 2.85 \text{ \AA}$).

Table 3. Data extracted from Gaussian fits of $\text{Ge}_{1-x}\text{Sn}_x$ $\theta/2\theta$ peaks of films grown on single crystal $\text{CaF}_2(111)$ and analyses: the lattice constant of each film determined by Bragg's law (a), the Sn alloying percentage (x) and the average out-of-plane diameter of the ordered regions of the corresponding crystalline orientation (D). Unless otherwise indicated, errors in peak position and FWHM are less than or equal to the step size of 0.001° .

Growth Temp. ($^\circ\text{C}$)	Peak Indices (hkl)	2θ ($^\circ$)	FWHM ($^\circ$)	a ($\text{\AA}$)	x (%)	D (nm)
250	(111)	27.072	0.031	5.700	5.05	293
300	(111)	27.073	0.028	5.700	5.05	330
350	(111)	27.079	0.028	5.699	4.93	239
400	(111)	27.076	0.022	5.699	4.93	413

Table 4. Data extracted from Gaussian fits of $\text{Ge}_{1-x}\text{Sn}_x$ $\theta/2\theta$ peaks of films grown on single crystal $\text{CaF}_2(100)$ with analyses: the lattice constant of each film determined by Bragg's law (a), the Sn alloying percentage (x) and the average out-of-plane diameter of the ordered regions of the corresponding crystalline orientation (D). Unless otherwise indicated, errors in peak position and FWHM are less than or equal to the step size of 0.001° . Relative intensity indicates the peak intensity relative to that of the film's (400) peak.

Growth Temp. ($^\circ\text{C}$)	Peak Indices (hkl)	2θ ($^\circ$)	FWHM ($^\circ$)	Relative Intensity	a ($\text{\AA}$)	x (%)	D (nm)
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250	---	---	---	---	---	---	---
	(400)	65.437	0.063	1	5.700	5.05	178
300	(111)	27.071	0.182	0.4	5.700	5.05	50
	(400)	65.445	0.070	1	5.700	5.05	150
350	(111)	27.127	0.163	9.0	5.689	---	56
	(400)	65.438	0.055	1	5.700	5.05	191
400	(111)	27.161	0.164	8.9	5.682	---	55
	(400)	65.441	0.068	1	5.700	5.05	198

Films grown on $\text{CaF}_2(111)$ exhibit only (111) peaks, as seen in Fig. 4(a), indicating that the out-of-plane growth direction of these films follows directly from that of the substrate. Likewise, films grown on $\text{CaF}_2(100)$ exhibit (400) peaks, shown in Fig. 4(c). In addition to this peak, however, these films also exhibit (111) peaks (Fig. 4(b)) indicating the existence of an additional orientation with an out-of-plane growth direction different from that of the substrate.

For pure Ge with a lattice constant of $5.658 \text{ \AA}$, the (111) and (400) peaks occur at 27.277° and 65.986° , respectively. The shifts in the exhibited $\text{Ge}_{1-x}\text{Sn}_x$ peaks from these positions to lower 2θ angles indicate an increase in lattice constant resulting from substitutional alloying of Sn atoms within the Ge lattice. By comparing the experimental calibration curves of the lattice constant of $\text{Ge}_{1-x}\text{Sn}_x$ vs. Sn concentration established by X-ray diffraction²² and Rutherford backscattering spectroscopy^{11, 23} with the lattice constants obtained from our $\text{Ge}_{1-x}\text{Sn}_x$ X-ray diffraction peaks, we can estimate the Sn concentrations (x) of each film. Furthermore, with the additional information of each $\theta/2\theta$ peak's FWHM we can estimate the average out-of-plane size of the ordered regions of each orientation. Here we use the approximation that the coherent size is inversely proportional to the peak broadening (after deconvolution with the instrument response function)²⁴:

$$D = \frac{\lambda}{\beta \cos \theta}. \quad (1)$$

D is the size of the ordered regions in the direction normal to the substrate, λ is the incident X-ray wavelength and β and θ are the deconvoluted FWHM and half the 2θ location of the corresponding XRD peak.

Up to 350°C the $\text{Ge}_{1-x}\text{Sn}_x(111)$ peaks exhibited by films grown on $\text{CaF}_2(111)$ are all similar in intensity, location, and broadening. At 400°C the $\text{Ge}_{1-x}\text{Sn}_x(111)$ peak develops a shoulder-like feature, skewing it toward higher values of 2θ . A schematic showing the broadening of the peak (filled red circle) and shoulder feature (open red oval) in reciprocal space (2θ and ω are the vertical and horizontal directions, respectively) is included as an inset in Fig. 4(a). ω broadening will be discussed shortly. The shoulder feature is an indication of the existence of regions within this sample that exhibits less lattice constant homogeneity than do the primary regions. For reasons to be discussed later in section D, we will refer to these as ‘type B regions.’ By fitting this peak with two Gaussians rather than one, we are still able to extract the necessary quantities for analysis of the primary orientation, which are comparable to those of the lower temperature samples. All films have similarly sized coherent vertical grains in the range of $293 - 413 \text{ nm}$, slightly lower than the film thickness of approximately 535 nm , and contain approximately 5% Sn. Up to 350°C no obvious trends in the data exist which suggests temperature has any noticeable effect on $\text{Ge}_{1-x}\text{Sn}_x$ alloy film's crystallization on single-crystal $\text{CaF}_2(111)$. Between

350 °C and 400 °C a critical temperature is reached, at which the growth of type B regions occurs. As will be discussed later in section D, the differences observed in the $\theta/2\theta$ scan of the 400 °C film may be due to the regions exhibiting type B epitaxy, or in-plane symmetry which mirrors that of the $\text{CaF}_2(111)$ substrate. The spatial confinement resulting from the existence of both orientations could potentially explain the observed peak broadening.

By changing the orientation of the substrate to (100) the deposited layer behaves dramatically differently. In these films the (400) peaks (see Fig. 4(c)) much like the (111) peaks of the films grown on $\text{CaF}_2(111)$, are nearly identical. They indicate consistent percentages of Sn alloying, also of about 5%, and vertical domain sizes in the range of 150 – 200 nm. At a growth temperature of 250 °C, (400) is the only peak exhibited by the film. Films grown at 300 °C and above, however, also display a (111) peak (Fig. 4(b)) revealing the existence of crystalline regions with an out-of-plane orientation different from (100) of the substrate. With increasing temperature the (111) peak grows in intensity, from noise level at 250 °C to approximately nine times the (400) peak intensity at 350 °C and 400 °C. In addition, the (111) peaks have FWHMs several times larger than those of the (400) peaks. The larger FWHMs of these peaks imply smaller coherent domains averaging approximately 50 – 60 nm in diameter (see Table 4). The (111) peaks are observed to exhibit a temperature-dependent shift toward higher 2θ values with increased growth temperature. It is possible this shift indicates a decrease in Sn alloying at higher temperatures; the lattice constants calculated from 2θ peak positions give alloying percentages of 3.73% and 2.77% for samples grown at 350 °C and 400 °C, respectively. However, EDS has revealed the chemical composition in each film to be nearly equivalent. A more likely explanation is higher compressive strain in the (111) oriented regions of the film layers grown at higher temperatures. A shift in the (111) peak has been shown to occur in $\text{Ge}_{1-x}\text{Sn}_x$ films grown on amorphous SiO_2 substrates for this reason²⁵. The derived values of Sn alloying percentage do not consider strain and thus are underestimates. Assuming $x \sim 0.0505$ we can estimate the strain perpendicular to the interface, $\varepsilon_{\perp}$:

$$\varepsilon_{\perp} = \frac{a_{\text{exp}} - a(\text{Ge}_{0.9495}\text{Sn}_{0.0505})}{a(\text{Ge}_{0.9495}\text{Sn}_{0.0505})}, \quad (2)$$

where a_{exp} is the experimentally determined lattice constant using Bragg's law (values for a_{exp} in Table 4 are 5.689 Å and 5.682 Å for 350 °C and 400 °C, respectively) and $a(\text{Ge}_{0.9495}\text{Sn}_{0.0505})$ is the lattice constant assuming 5.05% Sn alloying, 5.700 Å. This comes out to be approximately -0.19% and -0.32% in the (111) oriented regions of films grown on $\text{CaF}_2(100)$ at 350 °C and 400 °C, respectively, implying slight compressive strain in the (111) orientation.

To measure the films' out-of-plane dispersions (another quantity used to determine crystal quality), X-ray diffraction rocking curves (RCs) were acquired by fixing the locations of the X-ray source and detector on each 2θ peak and varying the incoming angle of the beam. This was done by rocking the sample about the horizontal axis perpendicular to the beam to record the diffracted FWHM. Symmetrical rocking curves were measured for each CaF_2 substrate peak and the $\text{Ge}_{1-x}\text{Sn}_x$ film peaks at $\chi \sim 0^\circ$, defining χ to be the out-of-plane angle from substrate normal perpendicular to the scattering plane. Minor adjustments in χ were made to account for slight misorientations ($< 1^\circ$) of the substrates' out-of-plane directions from [111] or [100]. The out-of-plane dispersions of the single-crystal substrates as quantified by RC FWHMs were approximately $0.029^\circ \pm 0.003^\circ$ for both the (111) and (100) oriented CaF_2 substrates. Table 5 includes the data from RCs of each film peak.

Table 5. Data extracted from Gaussian fits of $\text{Ge}_{1-x}\text{Sn}_x$ RC peaks and dislocation densities (D_{dis}) calculated therefrom. Unless otherwise indicated, errors in FWHM are less than or equal to the step sizes of 0.001° and 0.01° for the sharper and broader peaks, respectively.

Film	Growth Temp. ($^\circ\text{C}$)	Peak Indices (hkl)	FWHM ($^\circ$)	D_{dis} (cm^{-2})
$\text{Ge}_{1-x}\text{Sn}_x$ film / $\text{CaF}_2(111)$	250	(111)	0.028	3.38×10^7
	300	(111)	0.038	6.20×10^7
	350	(111)	0.028	3.38×10^7
	400	(111)	0.037	5.89×10^7
$\text{Ge}_{1-x}\text{Sn}_x$ film / $\text{CaF}_2(100)$	250	---	---	---
		(400)	0.029	3.61×10^7
	300	(111)	3.5 ± 0.1	$\sim 5 \times 10^{11}$
		(400)	0.035	5.27×10^7
	350	(111)	1.53	$\sim 8 \times 10^{10}$
		(400)	0.035	5.27×10^7
	400	(111)	1.24	$\sim 7 \times 10^{10}$
		(400)	0.029	3.61×10^7

The observed rocking curves of the $\text{Ge}_{1-x}\text{Sn}_x(111)$ peaks of samples grown on $\text{CaF}_2(111)$, shown in Fig. 5(a), have consistent FWHMs ($\sim 0.03^\circ$) independent of temperature. The inset of Fig. 5(a) shows the full range of the rocking curve (from -3° to 3°) taken of the film grown at 400°C . A much broader peak with FWHM of about 1.5° is seen, again corresponding to the open red oval in the reciprocal space schematic in the inset of Fig. 4(a). This behavior is not observed for samples grown at lower temperatures. To determine the origin of the broad peak, a second RC was taken with the beam and detector focused on the shoulder feature of the $\text{Ge}_{1-x}\text{Sn}_x(111)$ $\theta/2\theta$ peak (Fig. 4(a), red curve). The sharp peak was not observed when scanned in this configuration, thus we can conclude that it originates from the primary orientation in the film, while the broad peak is due to the aforementioned type B regions. RC peaks of the primary (400) orientations of the 400°C film and of each lower temperature sample have FWHMs ($\sim 0.03^\circ$) comparable to those of the substrate RC peaks, indicating high-quality epitaxy and single-crystal out-of-plane dispersions. In contrast when grown at 300°C on biaxial $\text{CaF}_2(111)$ nanorods $\text{Ge}_{1-x}\text{Sn}_x(111)$ film exhibited an out-of-plane dispersion of $10.8^\circ \pm 0.2^\circ$. As expected, reducing the out-of-plane dispersion of the starting substrate resulted in dramatically reduced dispersion in the film layer.

Fig. 5(b) shows the $\text{Ge}_{1-x}\text{Sn}_x(111)$ RCs of the films grown on $\text{CaF}_2(100)$. As expected from the $\theta/2\theta$ scans, the RC profiles grow in intensity with increasing growth temperature, staying approximately constant between 350°C and 400°C . In addition, we see that the peaks become narrower at higher temperatures. Relative to the $\text{Ge}_{1-x}\text{Sn}_x(111)$ RCs exhibited by the films grown on $\text{CaF}_2(111)$, the FWHMs of these peaks are two orders of magnitude larger. It is expected that $\text{Ge}_{1-x}\text{Sn}_x(111)$ grow with higher quality epitaxy (as quantified by dispersions) on (111) oriented CaF_2 than on $\text{CaF}_2(100)$. The in-plane lattice mismatch is much less between $\text{Ge}_{1-x}\text{Sn}_x(111)$ and $\text{CaF}_2(111)$ ($< 4\%$) than between $\text{Ge}_{1-x}\text{Sn}_x(111)$ and $\text{CaF}_2(100)$ ($\sim 13\%$). Furthermore, the in-plane symmetries match identically in the former case but not in the latter.

By the same line of reasoning it follows that the $\text{Ge}_{1-x}\text{Sn}_x(400)$ RCs shown in Fig. 5(c) have dispersions ($\sim 0.03^\circ$) not dissimilar to those of the $\text{CaF}_2(100)$ substrates. These peaks also vary little in intensity and are consistent with $\theta/2\theta$ results.

The broadening in a RC profile is due to the intrinsic imperfection of the sample material (*i.e.* deviation from perfectly parallel atomic planes). These additional broadenings could come from angular rotation at dislocations (mosaics tilted with respect to each), curvature, crystal size, and strain in the sample material. The instrument broadening is usually less than $0.005^\circ - 0.01^\circ$ and can be neglected. If we assume that the RC FWHM broadening is predominantly due to a network of misfit dislocations stemming from the lattice-mismatched interface between $\text{Ge}_{1-x}\text{Sn}_x$ films and CaF_2 substrates²⁶, the dislocation density of films can be estimated. The dislocation density, D_{dis} from the FWHM broadening β_{dis} has been derived as^{27, 28}

$$D_{dis} \approx \beta_{dis}^2 / (2\pi \ln(2)b^2) \approx \beta_{dis}^2 / (4.36 b^2), \quad (3)$$

where b is the length of the Burgers vector. For Ge (and thus for $\text{Ge}_{1-x}\text{Sn}_x$) the Burgers vector is $\frac{1}{2} [110]$ ²⁹. Using the experimentally derived lattice constants from Tables 3 & 4 yields Burgers vector lengths in the range of 0.4018 to 0.4031 nm for each sample. The calculated dislocation densities of each film's rocking curve are listed in the last column of Table 5. Note that because the other possible sources of RC broadening have been ignored, these provide upper limits to the dislocation densities.

The regions with out-of-plane orientation identical to that of the corresponding substrate ($\text{Ge}_{1-x}\text{Sn}_x(111)$ RCs of films on $\text{CaF}_2(111)$ and $\text{Ge}_{1-x}\text{Sn}_x(400)$ RCs of films on $\text{CaF}_2(100)$) exhibit D_{dis} on the order of 10^7 cm^{-2} independent of growth temperature. This is lower than values calculated using this method for high-quality GaAs grown on Si(001) of $\sim 10^8 \text{ cm}^{-2}$ ²⁸. Others have achieved semiconductor films with lower dislocation densities on the order of $10^5 - 10^6 \text{ cm}^{-2}$ in the near-surface regions of thicker epitaxial layers (over one micron)^{30, 31} due to the increase in strain relaxation with film layer thickness. It is likely that the dislocation densities in these $\text{Ge}_{1-x}\text{Sn}_x$ alloys could similarly be reduced by growing film layers thicker than the 535 nm layers grown in this study. The regions of samples grown on $\text{CaF}_2(100)$ substrates exhibiting (111) texture have dislocation densities several orders of magnitudes higher.

D. XRD pole figure analysis and in-plane texture evolution of $\text{Ge}_{1-x}\text{Sn}_x$ films on single crystal CaF_2

The in-plane epitaxial relationship between the deposited film and the substrate, as well as the existence of any additional rotational domains or crystal twinning can be revealed in an XRD pole figure. A pole figure is a compilation of in-plane azimuthal angular scans, or phi (ϕ) scans, of a Bragg peak at incrementally increasing chi (χ) angles spanning 0° to 90° with χ measured radially from the origin. Figs. 6 and 7 show experimental $\text{Ge}_{1-x}\text{Sn}_x(111)$ pole figures and theoretical models for films grown on $\text{CaF}_2(111)$ and $\text{CaF}_2(100)$, respectively, each taken at the 2θ locations indicated in Tables 3 and 4. Tick marks are placed along the edge of each pole figure to indicate the azimuthal location of the CaF_2 substrate poles (*i.e.* the substrate's in-plane symmetry). Theoretical $\text{Ge}_{1-x}\text{Sn}_x(111)$ pole figures indicating [111] and [100] out-of-plane growth directions with one rotational orientation and with no twinning are shown in Figs. 6(e) and 7(e), respectively. In a (111) pole figure taken of a (111) oriented single crystal there exist

four $\{111\}$ poles, one of which is along the surface normal direction, $[111]$. The three outer poles are separated by 120° in ϕ and located at $\chi \sim 70^\circ$ (Fig. 6(e)). A (111) pole figure taken of a (100) oriented single crystal exhibits four $\{111\}$ poles, none of which is along the surface normal direction. They are each located at $\chi \sim 55^\circ$ and are 90° apart in ϕ (Fig. 7(e)).

a. Films grown on $\text{CaF}_2(111)$

Up to a growth temperature of 350°C films grown on $\text{CaF}_2(111)$ exhibit straight-forward pole figures containing an intense center pole as well as three outer poles, which lie at ϕ and χ locations identical to those of the substrate ($\chi \sim 70^\circ$). These are a clear indication of a (111) oriented single crystal film with no crystal twinning. At 400°C the film exhibits an additional set of three poles at $\chi \sim 70^\circ$ as well as twelve poles at $\chi \sim 56^\circ$, six poles at $\chi \sim 38^\circ$ and twelve poles at $\chi \sim 22^\circ$. The second set of three poles at $\chi \sim 70^\circ$ indicates the existence of different crystalline regions within the film, which is consistent with the differences observed $\theta/2\theta$ and rocking curve scans of this sample, as previously discussed. It can now be further determined that the second regions exhibit type B epitaxy (*i.e.* its in-plane symmetry mirrors that of the CaF_2 substrate). The remaining poles are illustrated in the primary and secondary twinning schematics shown in Figs. 6(f) and 6(g), respectively. As illustrated for the $(1\bar{1}1)$ pole in Fig. 6(f) each $\{111\}$ outer pole has three primary twin poles (filled red circles): two located at $\chi \sim 56^\circ$, labeled $T(\bar{1}\bar{1}1)$ and $T(1\bar{1}\bar{1})$, and one at $\chi \sim 38^\circ$ labeled $T(\bar{1}\bar{1}\bar{1})$. The primary twin poles originate from crystal twins formed during growth or annealing with in-plane symmetry rotated 180° about the out-of-plane direction of the corresponding primary pole ($[1\bar{1}1]$ in the schematic). In addition, each primary twin pole at $\chi \sim 56^\circ$ has one secondary twin pole at $\chi \sim 22^\circ$ as shown in Fig. 6(g), labeled $TT(11\bar{1})$ and $TT(\bar{1}\bar{1}1)$ (filled blue circles). These were generated by a second rotation of 180° about the out-of-plane direction of the corresponding twin pole, $T(\bar{1}\bar{1}1)$ or $T(1\bar{1}\bar{1})$. Fig 6(h) shows the primary poles, primary twin poles and secondary twin poles combined for one rotational orientation. The theoretical pole figure in Fig. 6(i) includes the type B orientation rotated 60° with respect to the first about $[111]$ and the primary and secondary twin poles thereof (all shown as open circles), which agrees well with the experimental data shown in Fig. 6(d).

Near 400°C the F layer on the substrate surface begins depleting. Density functional theory calculations predict that this causes Ge atoms to bond to the exposed Ca^{2+} ions, yielding type B epitaxy³². The existence of both type A and type B epitaxies indicates that the top F layer is only partially depleted. Type B epitaxy has been reported for pure Ge grown on biaxial CaF_2 at 400°C ¹³. This depletion does not occur at lower growth temperatures, explaining the existence of the type B orientation in only the 400°C sample. The films grown on $\text{CaF}_2(111)$ at lower temperatures exhibit higher-quality epitaxy. This is reflected by the identical location of the $\text{Ge}_{1-x}\text{Sn}_x\{111\}$ poles to the location of the substrate. The sharpness of these poles indicates single-crystal in-plane dispersions in addition to the already determined single-crystal out-of-plane dispersions.

We can infer a direct in-plane epitaxial relationship between each film and each substrate: $\langle 1\bar{2}1 \rangle_{\text{Film}} \parallel \langle 1\bar{2}1 \rangle_{\text{CaF}_2}$ and $\langle \bar{1}01 \rangle_{\text{Film}} \parallel \langle \bar{1}01 \rangle_{\text{CaF}_2}$. The type B epitaxy exhibited in the 400°C sample is rotated 60° with respect to the first about $[111]$.

b. Films grown on $\text{CaF}_2(100)$

Films grown on (100) oriented CaF_2 substrates demonstrate a temperature-dependent evolution of in-plane epitaxy (see Figs. 7(a) – (d)). Each pole figure contains peaks which indicate a superposition of [100] and [111] growth directions. The population of the (111) orientation (the poles of which were previously discussed) is nearly zero in the film grown at 250 °C but dominant in the films grown at 350 °C and 400 °C. These results are consistent with $\theta/2\theta$ results, which have also indicated this temperature-dependent evolution. The poles indicating [100] out-of-plane are described in Figs. 7(e) – (i). Much like the film grown on $\text{CaF}_2(111)$ at 400 °C, the (100) orientation of each film grown on $\text{CaF}_2(100)$ exhibits two sets of {111} poles which indicate [100] out-of-plane. The first set occurs at azimuthal locations identical to those of the substrate {111} peaks, while the second set is rotated 45° about [100] with respect to the first. Each primary {111} pole ($\chi \sim 55^\circ$) has one primary twin pole located at $\chi \sim 16^\circ$ (filled red circle labeled $T(\bar{1}11)$ in Fig. 7(f)), each of which has two secondary twin poles at $\chi \sim 63^\circ$ (filled blue circles labeled $TT(\bar{1}\bar{1}1)$ and $TT(1\bar{1}\bar{1})$ in Fig. 7(g)). All together these yield the schematic in Fig. 7(h). Adding a second orientation (*i.e.* a second set of primary poles at $\chi \sim 55^\circ$ rotated 45° in ϕ about [100] with respect to the first) gives Fig. 7(i), which accurately describes the poles contributing to [100] out-of-plane in each of the experimental pole figures. Much like the previously discussed case of $\text{Ge}_{1-x}\text{Sn}_x(111)$ on $\text{CaF}_2(111)$, the second set of poles is likely due to type B epitaxy resulting from some level of depletion of the top F⁻ layer. It appears, however that this depletion occurs as low as 250 °C on the (100) face compared to near 400 °C for the (111) face. Because the type B poles are much weaker than the type A poles, we conclude that the F⁻ depletion is also much less complete than on the (111) face resulting in a lower population of the type B orientation. We can infer a direct in-plane epitaxial relationship between the primary (100) domain of each film and each substrate: $\langle 010 \rangle_{\text{Film}} // \langle 010 \rangle_{\text{CaF}_2}$ and $\langle 001 \rangle_{\text{Film}} // \langle 001 \rangle_{\text{CaF}_2}$. The type B orientation is rotated 45° about [100] with respect to the primary.

More interesting is the origin behind the remaining poles, which indicate [111] out-of-plane and depend heavily on growth temperature. As previously discussed, a (111) oriented single crystal exhibits three outer primary {111} poles located at $\chi \sim 70^\circ$ and spaced 120° apart in ϕ (as in Fig. 6(e)). In the pole figures of films grown on $\text{CaF}_2(100)$ (most notably those grown at 350 °C and 400 °C), twelve spots rather than three are observed, which implies the existence of four rotational domains with [111] out-of-plane. This is illustrated in Fig 8. $\text{Ge}_{1-x}\text{Sn}_x$ atoms, shown as open green circles, are superimposed onto the $\text{CaF}_2(100)$ lattice, shown as filled orange circles. Arrows indicated the azimuthal locations of the primary {111} poles generated by each configuration. Theoretical models of the poles due to each rotational domain are included beneath. As before, filled green circles represent primary {111} poles, while filled red circles are twin poles (see Fig. 6(f) for further description). No secondary twin poles are observed. Additional domains rotated 30°, 60° and 90° about [111] relative to the first each give rise to an additional set of poles. The sum of the first four models yields the fifth (Fig. 8(e)), which accurately describes the poles due to [111] out-of-plane observed in the experimental pole figures. A weighted superposition of the fifth model and the poles indicating [100] out-of-plane (Fig. 7(i)) completely describes the experimental pole figures of films grown on $\text{CaF}_2(100)$ shown in Figs. 7(a) – (d). The in-plane epitaxial relationships for the first (111) domain and the substrate are $\langle 1\bar{2}1 \rangle_{\text{Film}} // \langle 011 \rangle_{\text{CaF}_2}$ and $\langle \bar{1}01 \rangle_{\text{Film}} // \langle 01\bar{1} \rangle_{\text{CaF}_2}$ (note that this can equivalently be written: $\langle 1\bar{1}0 \rangle_{\text{Film}} // \langle 011 \rangle_{\text{CaF}_2}$ and $\langle \bar{1}01 \rangle_{\text{Film}} // \langle 01\bar{1} \rangle_{\text{CaF}_2}$). The remaining (111) domains are rotated 30°, 60° and 90° about [111] with respect to the primary.

A simple superlattice area matching model was used to gain a qualitative understanding of the observed heteroepitaxy^{33, 34}. Minimization of superlattice area and area mismatch were calculated for each of the possible epitaxies of $\text{Ge}_{1-x}\text{Sn}_x(111)$ on $\text{CaF}_2(100)$ by inputting the geometry of each plane (unit vector lengths and the intermediate angle). Superlattice area A is defined as the area in which a coincidence lattice occurs between the overlayer and the substrate. Superlattice area mismatch ΔA is defined as the area over which the film superlattice unit and substrate superlattice unit do not overlap and is given by

$$\Delta A = A \left[\left(\frac{\Delta a}{a} \right) + \left(\frac{\Delta b}{b} \right) + \Delta \alpha \cot \alpha \right], \quad (4)$$

where a and b are the superlattice lengths separated by angle α , and Δa , Δb and $\Delta \alpha$ are the differences in each parameter between the film and substrate. Superlattice area mismatch (ΔA) is directly proportional to superlattice area (A), thus small superlattice areas in addition to small mismatches between the superlattice lengths and angles of the film and substrate are favorable. The constraints used were the maximum area limit of each superlattice ($200 \text{ \AA}^2$) and the maximum allowable mismatch between the superlattice lengths and superlattice angles of $\text{Ge}_{1-x}\text{Sn}_x$ and CaF_2 (10% each). The results are shown in Table 6.

Table 6. Superlattice area matching results for $\text{Ge}_{1-x}\text{Sn}_x(111)$ on $\text{CaF}_2(100)$.

Epitaxial Condition ($\text{Ge}_{1-x}\text{Sn}_x // \text{CaF}_2$)	Superlattice Length ($\text{Ge}_{1-x}\text{Sn}_x/\text{CaF}_2$)		Superlattice Angle ($^\circ$)		Superlattice Area ($\text{\AA}^2$)		Area Mismatch ($\text{\AA}^2$)
	a ($\text{\AA}$)	b ($\text{\AA}$)	$\text{Ge}_{1-x}\text{Sn}_x$	CaF_2	$\text{Ge}_{1-x}\text{Sn}_x$	CaF_2	
$[1 \bar{1} 0] // [0 1 1]$	8.06 / 7.72	8.06 / 8.64	60.00	63.43	56.26	59.66	8.31
$[1 \bar{1} 0] // [0 1 3]$	8.06 / 8.64	13.96 / 13.92	90.00	82.87	112.52	119.34	8.33
$[3 \bar{2} \bar{1}] // [0 1 1]$	10.67 / 10.92	14.53 / 13.92	87.00	78.69	154.82	149.06	11.42
$[1 \bar{1} 0] // [0 0 1]$	12.09 / 10.92	14.53 / 13.92	73.90	78.69	168.78	149.06	27.49
$[1 \bar{1} 0] // [0 1 2]$	12.09 / 12.21	14.53 / 13.92	73.90	74.74	168.78	163.97	9.47
$[3 \bar{2} \bar{1}] // [0 0 1]$	10.67 / 10.92	16.12 / 17.27	79.11	71.57	168.90	178.92	20.38

The observed epitaxy of $\text{Ge}_{1-x}\text{Sn}_x(111)$ on $\text{CaF}_2(100)$ ($\langle 1\bar{1}0 \rangle_{\text{Film}} // \langle 011 \rangle_{\text{CaF}_2}$), which generates the four rotational domains seen in experimental pole figures (and shown in Fig. 8) is shown in row 1 of Table 6. It has both the lowest superlattice area as well as the lowest superlattice area mismatch. Similar geometrical matching has been observed in other heteroepitaxial systems such as $\text{CdTe}(111)$ on $\text{Ni}(100)$ ^{35, 36}.

Of note, this superlattice area matching model was also used to predict the epitaxies of $\text{Ge}_{1-x}\text{Sn}_x(111)$ on $\text{CaF}_2(111)$ and $\text{Ge}_{1-x}\text{Sn}_x(100)$ on $\text{CaF}_2(100)$. These calculations returned the observed parallel epitaxial relationships as those being the most favorable and are not included for brevity.

The number of equivalent rotational domains N_{RD} on a substrate in a heteroepitaxy system can be qualitatively determined using the symmetries of the epitaxial layer and the substrate with respect to the substrate normal. A unified theory of the minimum number of epitaxially equivalent rotational domains has been proposed using group theory^{37, 38}. The minimum number of rotational domains exhibited in a heteroepitaxial system (N_{RD}) is

$$N_{RD} = \text{lcm}(n, m) / m, \quad (4)$$

where $lcm(n,m)$ indicates the lowest common multiple of m and n , which describe the symmetries of the epitaxial layer and the substrate surface, respectively (the epitaxial layer and substrate surface have symmetries C_m and C_n , respectively). $\text{Ge}_{1-x}\text{Sn}_x(111)$ and $\text{Ge}_{1-x}\text{Sn}_x(100)$ have the same invariant 2D point symmetries as $\text{CaF}_2(111)$ and $\text{CaF}_2(100)$, respectively, thus the value of N_{RD} is each of these epitaxial systems is 1. In each case, we observe one rotational domain. For $\text{Ge}_{1-x}\text{Sn}_x(111)$ on $\text{CaF}_2(100)$, $m = 3$ and $n = 4$, so four rotational domains are predicted, as is also consistent with our observation.

Many results by others have revealed the dependence of film texture on temperature^{8, 39, 40}. The existence of (111) oriented $\text{Ge}_{1-x}\text{Sn}_x$ grown on single crystal $\text{CaF}_2(100)$ has not previously been reported. This also has not been seen in the literature for pure Ge films grown on single crystal $\text{CaF}_2(100)$. Furthermore, no results in the literature were found which reported crystallization of pure Ge films at temperatures as low as 250 °C. Ge films were reported by Barkai *et al.*²⁶ and Snow *et al.*⁴¹ to be grown at comparably-low growth temperatures, but they were amorphous. Pundsack⁴² determined the amorphous to crystalline transition for pure Ge on single crystal $\text{CaF}_2(111)$ to occur in the range of 320 °C to 400 °C, with the single-crystal texture exhibited in films grown at between 500 °C and 600 °C, temperatures far higher than shown here. For Ge films grown on amorphous carbon, an *in situ* TEM study of the annealing of the initially amorphous Ge film shows that the crystallization temperature is even higher, at 650 °C, and that the activation energy for homogeneous nucleation is up to about 3.1 eV⁴³. Our observed lower crystallization temperature exhibited by $\text{Ge}_{1-x}\text{Sn}_x$ films is due to the surfactant role of Sn, which increases the diffusion of Ge adatoms^{20, 44}.

E. Hall mobility of $\text{Ge}_{1-x}\text{Sn}_x$ films on single crystal $\text{CaF}_2(111)$

To measure the dependence of the films' electrical properties on growth temperature, room temperature Hall mobility measurements were conducted. The obtained parameters are included in Table 7.

Table 7. Hall mobility data: type of charge carriers, hole Hall mobility (μ_h), resistivity (ρ) and charge carrier concentration ($N_A - N_D$).

Film	Growth Temp. (°C)	Type	μ_h ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	ρ ($\times 10^{-2} \Omega\text{-cm}$)	$N_A - N_D$ ($\times 10^{18} \text{cm}^{-3}$)
$\text{Ge}_{1-x}\text{Sn}_x / \text{CaF}_2(111)$	250	p	36.6	1.92	8.9
	300	p	53.6	2.10	5.55
	350	p	74.3	2.08	4.04
	400	p	89.9	2.46	2.83
$\text{Ge}_{1-x}\text{Sn}_x / \text{CaF}_2(100)$	250	p	30.3	1.92	8.88
	300	p	61.5	2.05	4.95
	350	p	89.4	2.37	2.95
	400	p	101.9	3.56	1.72

Each film is determined to be p-type. Hole Hall mobility (μ_h) and resistivity (ρ) of films increase with increasing growth temperature while charge carrier concentration (the density of acceptors, N_A , minus the density of donors, N_D) shows the opposite trend. Each is independent of substrate orientation.

This inverse relationship between Hall mobility and doping levels is consistent with results for bulk p-type Ge⁴⁵ as well as Ge_{1-x}Sn_x films grown by atmospheric pressure CVD on Ge(001)⁴⁶ and grown by UHV CVD Si(100)⁴⁷ substrates. Like the results of Vincent *et al.* our values of Hall mobility are lower than those for p-Ge indicating the possibility of alloy scattering in our films. In addition to this, impurity scattering occurs due to the high impurity concentration in our films, which further reduces mobility. Because in our films the charge carriers come not from Sn alloying but from impurities unintentionally introduced during the deposition process (notably C, H and O), our mobility values are less than those reported by Vincent *et al.* and Xie *et al.* (by factors of approximately 2 – 6). In each of the cited studies, films were intentionally doped with either B, P or As. It is worth noting that pure Ge films deposited onto single crystal CaF₂(111) by a similar method as that reported herein exhibited similar values for both hole concentration and Hall mobility⁴².

Resistivity of films increases with growth temperature due to the simultaneous increase in hole charge carrier concentration. This, too has been shown to occur in p-Ge⁴⁸ although our values are about one order of magnitude higher. Commercial-grade UHV systems and other growth methods such as electron beam evaporation can achieve significantly lower levels of contamination and could expect to generate improved mobility in Ge_{1-x}Sn_x films.

Conclusion

Ge_{1-x}Sn_x films with ~ 5% Sn were successfully grown on CaF₂ films with both (111) and (100) orientations at temperatures below the crystallization temperature of pure Ge. We have shown via SEM, AFM, EDS, and several X-ray diffraction analysis methods that although morphologically and chemically similar, the texture of the two films at each growth temperature is dramatically different. High-quality Ge_{1-x}Sn_x(111) films were grown on CaF₂(111) with in- and out-of-plane dispersions quantitatively comparable to those of the substrate. The quality of these films is far better than that of Ge_{1-x}Sn_x(111) grown on biaxial CaF₂(111) nanorods under similar conditions due to the decreased substrate dispersions. Although the film exhibits twinning when grown at 400 °C, the epitaxy otherwise follows directly from the substrate. No twinning was seen in samples grown below 400 °C. In contrast, XRD pole figure analysis revealed that Ge_{1-x}Sn_x grown on (100) oriented CaF₂ exhibits a superposition of both (111) and (100) orientations. At 250 °C and 300 °C growth temperatures the (100) orientation dominates, while the (111) orientation was dominant in samples grown at 350 °C and 400 °C. Although the dispersions of the (111) orientation are quite large, the (100) orientation exhibits in- and out-of-plane dispersions similar to those of the substrate. The growth temperature yielding the best crystallization was found to be in the range of 250 °C to 350 °C for films grown on CaF₂(111) and 350 °C for films grown on CaF₂(100). These are far lower than the optimal crystallization temperature reported between 500 °C and 600 °C for pure Ge on single crystal CaF₂(111).

Morphology and electrical properties of films were also shown to be growth temperature-dependent. Vertical roughness and lateral feature size increase with growth temperature, as do Hall mobility and electrical resistivity. Charge carrier concentration of films showed the opposite trend.

The high-quality crystallinity of these samples makes this film an attractive candidate for a variety of applications. Because Sn serves to lower the crystallization temperature of Ge, our simple growth method could reduce the energy costs needed for production of Ge films by alloying with low percentages of Sn. The combination of these results with the previous knowledge as to the tunable nature of the $\text{Ge}_{1-x}\text{Sn}_x$ band gap indicates that $\text{Ge}_{1-x}\text{Sn}_x$ films has potential for use in optoelectronic devices including, but not limited to, those which currently utilize pure Ge.

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Figure 1. Schematic outlining the growth procedure (not to scale). (a) Bare CaF_2 substrate; (b) Deposition of approximately 35 nm layer of Sn at room temperature; (c) Deposition of approximately 500 nm layer of Ge with the substrate temperature elevated via resistive heating; (d) Post-deposition annealing at growth temperature for one hour to improve film uniformity and crystallinity.

Figure 2. SEM images of: (a) – (d) films grown on CaF₂(111) substrates at 250 °C, 300 °C, 350 °C and 400 °C; (e) – (h) films grown on CaF₂(100) substrates at 250 °C, 300 °C, 350 °C and 400 °C. AFM images ($2 \times 2 \mu\text{m}$) of each sample are included as insets. The $1 \mu\text{m}$ scale bars apply to both SEM images and AFM scans.

Figure 3. TEM/EDS of $\text{Ge}_{1-x}\text{Sn}_x$ film grown on $\text{CaF}_2(111)$ substrate at 400 °C: (a) Cross-sectional TEM image (scale bar indicates 200 nm). (b) EDS data collected across the $\text{Ge}_{1-x}\text{Sn}_x$ film thickness profile. Distances are measured from the $\text{CaF}_2/\text{Ge}_{1-x}\text{Sn}_x$ interface. Inset: EDS composition spatial mapping (scale bar indicates 40 nm). (c) HRTEM image of $\text{Ge}_{1-x}\text{Sn}_x$ film (scale bar indicates 3 nm). Inset: SADP of $\text{Ge}_{1-x}\text{Sn}_x$ film (scale bar indicates 3 nm^{-1}).

Figure 4. XRD $\theta/2\theta$ scans of: (a) $\text{Ge}_{1-x}\text{Sn}_x(111)$ peaks of films grown on $\text{CaF}_2(111)$ substrates; (b) $\text{Ge}_{1-x}\text{Sn}_x(111)$ peaks of films grown on $\text{CaF}_2(100)$ substrates; (c) $\text{Ge}_{1-x}\text{Sn}_x(400)$ peaks of films grown on $\text{CaF}_2(100)$ substrates. Inset of (a): Reciprocal space schematic (not to scale) showing the 2θ and ω broadenings of the $\text{Ge}_{1-x}\text{Sn}_x(111)$ peak in the sample grown on $\text{CaF}_2(111)$ at 400 °C. The filled red circle represents the primary (111) peak, while the open red oval is the (111) peak due to the type B regions.

Figure 5. XRD rocking curve (RC) scans of: (a) $\text{Ge}_{1-x}\text{Sn}_x(111)$ peaks of films grown on $\text{CaF}_2(111)$ substrates; (b) $\text{Ge}_{1-x}\text{Sn}_x(111)$ peaks of films grown on $\text{CaF}_2(100)$ substrates; (c) $\text{Ge}_{1-x}\text{Sn}_x(400)$ peaks of films grown on $\text{CaF}_2(100)$ substrates. The inset of (a) shows the full range of the $\text{Ge}_{1-x}\text{Sn}_x(111)$ RC taken of the sample grown on $\text{CaF}_2(111)$ at 400 °C. This was the only sample to exhibit a double-peak.

Figure 6. (a) – (d): Experimental XRD $\text{Ge}_{1-x}\text{Sn}_x(111)$ pole figures of films grown on $\text{CaF}_2(111)$ substrates at 250 °C, 300 °C, 350 °C and 400 °C. (e) Theoretical $\text{Ge}_{1-x}\text{Sn}_x(111)$ pole figure for $[111]$ out-of-plane with no twinning. (f) Configuration of the primary twin poles of the $(1\bar{1}\bar{1})$ pole, labeled $T(\bar{1}\bar{1}\bar{1})$, $T(\bar{1}\bar{1}\bar{1})$ and $T(\bar{1}\bar{1}\bar{1})$. (g) Configuration of the secondary twin poles of the $(1\bar{1}\bar{1})$ pole, or twins of $T(\bar{1}\bar{1}\bar{1})$ and $T(1\bar{1}\bar{1})$, labeled $TT(\bar{1}\bar{1}\bar{1})$ and $TT(1\bar{1}\bar{1})$, respectively. (h) Full twinning configuration for $[111]$ out-of-plane with one rotational domain. (i) Full twinning configuration for $[111]$ out-of-plane with two rotational domains, the second rotated 60° about $[111]$ with respect to the first and shown using open circles (compare with (d)). Tick marks are included along the outside of each experimental pole figure to indicate the azimuthal position of the substrate peaks.

Figure 7. (a) – (d): Experimental XRD $\text{Ge}_{1-x}\text{Sn}_x(111)$ pole figures of films grown on $\text{CaF}_2(100)$ substrates at 250 °C, 300 °C, 350 °C and 400 °C. (e) Theoretical $\text{Ge}_{1-x}\text{Sn}_x(111)$ pole figure for $[100]$ out-of-plane with no twinning. (f) Configuration of the primary twin pole of the (111) pole, labeled $T(\bar{1}\bar{1}1)$. (g) Configuration of the secondary twin poles of the (111) pole, or twins of $T(\bar{1}\bar{1}1)$, labeled $TT(\bar{1}\bar{1}\bar{1})$ and $TT(1\bar{1}\bar{1})$. (h) Full twinning configuration for $[100]$ out-of-plane with one rotational domain. (i) Full twinning configuration for $[100]$ out-of-plane with two rotational domains, the second rotated 45° about $[100]$ with respect to the first and shown using open circles. Note that no additional secondary twins appear in (i) relative to (h) due to overlapping. Experimental pole figures shown in (a) – (d) exhibit a temperature-dependent weighted superposition of multiple sets of (100) and (111) out-of-plane orientations. Tick marks are included along the outside of each experimental pole figure to indicate the azimuthal position of the substrate peaks.

Figure 8. Schematic illustrating the four rotational domains of $\text{Ge}_{1-x}\text{Sn}_x(111)$ on $\text{CaF}_2(100)$. $\text{Ge}_{1-x}\text{Sn}_x$ atoms are shown as open green circles superimposed on the $\text{CaF}_2(100)$ unit mesh, shown as filled orange circles. The $\text{Ge}_{1-x}\text{Sn}_x$ unit meshes in (b), (c) and (d) are rotated 30° , 60° and 90° about $[111]$ relative to (a), as indicated. Arrows indicate the azimuthal locations of primary $\{111\}$ poles generated from each configuration. Theoretical models of pole figures generated by each rotational domain are included beneath each schematic. (e) is the sum of the models in (a) – (d), showing all of the poles due to $[111]$ out-of-plane exhibited by samples grown on $\text{CaF}_2(100)$.