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Low Temperature (375°C) Metal Induced Lateral Crystallization (MILC) of $Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) using Silicide/Germanide Forming Metals (Ni, Pd and Co)

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1. Introduction:

Re-crystallization of a-SiGe on insulator may open up many potential applications: Ge rich SiGe in photodetector of 1.3 and 1.55 μm communication wavelengths, thin film tandem solar cell; Ge in three-dimensional ICs and TFT. To be integrated on top of existing devices or cheap substrates, SiGe should be crystallized at low temperature, preferably below 400°C. Metal Induced (Lateral) Crystallization (MIC/MILC) technique is known to substantially reduce crystallization temperature of Si [1] and Ge [2]. The metals used in MILC process can be categorized into two groups: the first (Co, Ni, Pd …) forms silicide/germanide and the second (Au, Ag, Al …) creates eutectic with SiGe. Focusing on the first metal group, we carried out low temperature (375°C) MILC of $Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) using Co, Ni and Pd. We analyzed and compared the MILC rates and crystal quality of the crystallized SiGe films for different Ge concentrations and seed metals. To our knowledge, such comparison has not been reported. Our attention was on Ge rich SiGe due to above listed applications. Optical microscope, Raman specstrocopy and AFM were used to characterize the annealed samples.

2. Experiment:

Fig. 1 illustrates the process steps used in this study. Roughly 50 nm thick $Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) layers were deposited on 400 nm thick SiO_2 by RF co-sputtering and patterned with lithography. Photoresist (PR) was then spin-coated and developed to open up seed metal windows. Ni, Co and Pd with thickness of about 4 nm were evaporated by e-beam. In control samples, no metal was deposited. Lift off was carried out, in which PR and metals except at window opening were removed in acetone solution that was subjected to ultrasonic treatment. The samples were then annealed for 3 hours at 375°C in N_2 ambient.

3. Results and discussions:

Contrast between MIC, MILC and amorphous region on the samples can be observed by optical microscope. An image of Ge (Pd) sample is shown in Fig. 2. The MILC lengths of varied Ge mole fractions for 3 seed metals, defined as perpendicular distance from MIC region to MILC amorphous interface, are compiled in Fig. 3. It can be seen that for Ni and Co, MILC lengths of $Si_{1-x}Ge_x$ drop with decreasing x, while for Pd, MILC length peaks at x=0.7. MILC process involves 3 steps: (1) Silicon Germanide formation, (2) diffusion of metal alloy and (3) reaction of metal alloy with amorphous SiGe resulting in crystallized SiGe. The rates of process (1) and (2) reduce with Ge mole fraction, due to higher alloying temperature and lower metal diffusivity. This explains the trend for Ni and Co. For Pd, we believe that rate of process (3) decreases with increasing Ge percentage, due to rising lattice mismatch between $Pd_2(SiGe)$ facets and SiGe planes. $Pd_2Si(0001)//Si(111)$ and $Pd_2Ge(0001)//Ge(111)$ with lattice mismatches of -2.36% [3] and -3.15% respectively. Thus for Pd samples, MILC rate is probably controlled by process (3) for Ge% > 0.7 and by process (1) and (2) for Ge% < 0.7.

Raman spectra of MIC and MILC Ge are shown in Fig. 4 and Fig. 5 respectively. The control Ge sample with no seed metal is still amorphous. Non-linear Lorentzian fitting of MIC Ge spectra shows no amorphous peak, indicating that the MIC Ge films are fully crystallized. Compared to Ni and Pd, Co induces higher quality MIC Ge but shorter MILC length. The former is probably due to small lattice mismatch between $CoGe_2$ and Ge [4], while the later is due to Co's low diffusivity in Ge [5]. Using the peak shifts from 300.5 cm^{-1} (bulk c-Ge phonon peak), the in-plane tensile strain $\varepsilon_{\parallel}$ in MIC, MILC Ge regions are calculated using the formula: $\Delta\omega = -415\varepsilon_{\parallel}$ [6] and tabulated in Table 1. Raman scattering spectra of MIC $Si_{0.3}Ge_{0.7}$ in Fig. 6 shows that Co MIC film is weakly crystallized. Ni MIC's blunt SiGe peak suggests that crystalline fraction of MIC $Si_{0.3}Ge_{0.7}$ induced by Ni is lower than by Pd.

It can be seen from Fig. 7 that rms roughnesses of MILC regions are similar to amorphous regions, and smaller than MIC regions. Looking at Ge MIC regions, there seems to be a correlation between surface roughness and Raman peak's FWHM: sharper peak, smaller roughness. Surface of MIC Ge by Co is as smooth as deposited amorphous Ge.

MILC lengths in fin structures of Ge and $Si_{0.3}Ge_{0.7}$ samples using Pd as metal seed, some of which are shown in Fig. 2, at different fin's width were measured and presented in Fig. 8. As the width decreases, the length increases to a maximum value, after which it drops. With smaller width, the diffusion path of metal alloy is more aligned, resulting in longer diffusion length. However, reducing the width also lessens metal's concentration, which limits MILC growth when the structure's width is below certain value.

4. Conclusions:

MILC of $Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) using Ni, Co and Pd were carried out at 375°C. Ni and Co MILC lengths decrease with reducing Ge fractions, while Pd MILC length peaks at Ge fraction of 0.7. For MIC of Ge, Co is a better seed metal among three metals studied, because Co induces crystalline film with not only higher quality but also smoother surface. Ge in MIC and MILC region experiences tensile strain of about 0.7% and 0.1% respectively. In term of MILC length, Pd performs similarly with Ni for Ge, and much better than Ni and Co for $Si_{0.3}Ge_{0.7}$. It is also shown that the MILC length depends on structure's width.

Table 1: Ge-Ge Raman peaks of MIC/ MILC poly Ge with different seed metals, and their corresponding tensile strain.

$(\omega\text{-}300.5) = -415\varepsilon_{\parallel}$	MIC			MILC	
	Co	Pd	Ni	Pd	Ni
ω (Ge-Ge) (cm^{-1})	297.9	297.7	297.6	300.1	300.0
$\varepsilon_{\parallel}$	0.63%	0.67%	0.70%	0.10%	0.12%

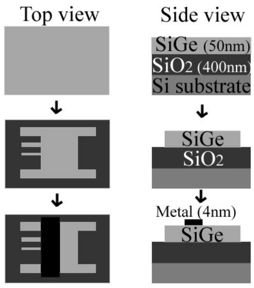

Fig.1 : Process steps.

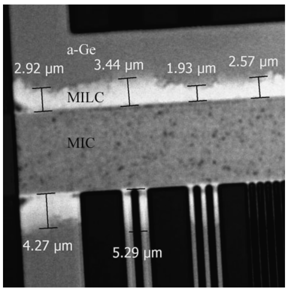

Fig. 2: Optical image of MILC Ge using Pd as metal seed.

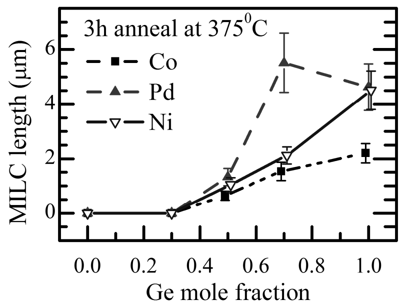

Fig. 3: MILC length of SiGe at different Ge mole fraction with Co, Pd and Ni as seed metals. 50 measurements were done for each mole fraction.

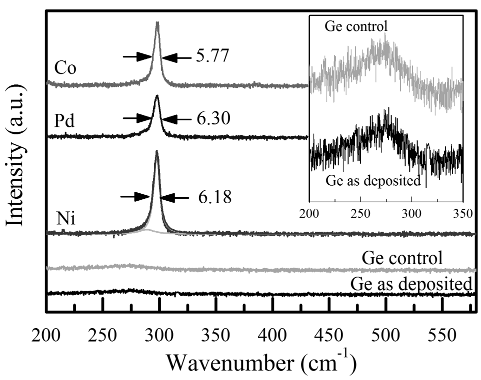

Fig. 4: Raman scattering spectra of MIC Ge. Inlet: Spectra of Ge control and as deposited Ge.

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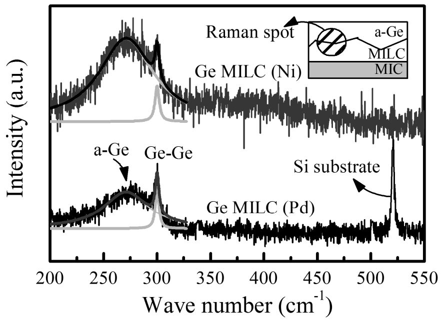

Fig. 5: Raman scattering spectra measured at Ge MILC/amorphous interface for Ni and Pd MILC. Laser spot's diameter is about 5μm.

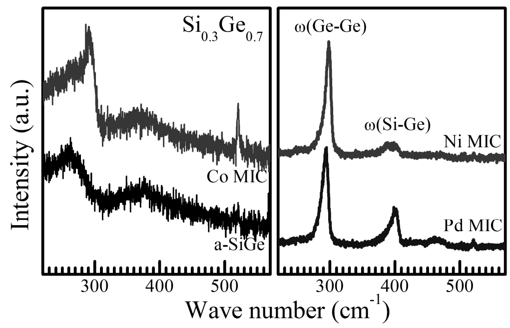

Fig. 6: Raman scattering spectra of MIC $Si_{0.3}Ge_{0.7}$.

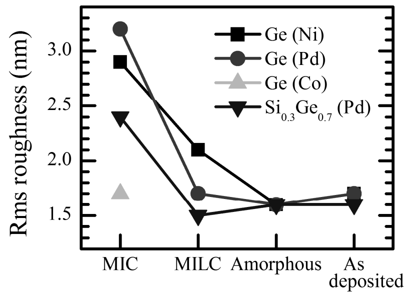

Fig. 7: RMS roughness of MIC/MILC and amorphous Ge and $Si_{0.3}Ge_{0.7}$ with different metal seeds.

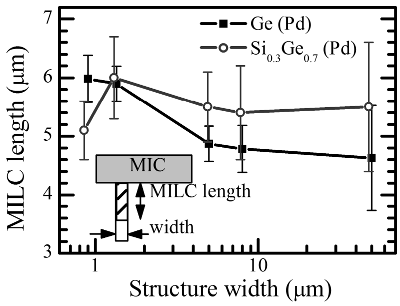

Fig. 8: MILC length at diferent fin structure's width.