

Phase transition and phonon dynamics in NiPdSi: An annealing study by temperature-dependent Raman spectroscopy

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We have demonstrated the effective Raman spectroscopy for the phase transition and phonon dynamics of NiPdSi films annealed at various temperatures. In addition to the appearance of alloy disorder-induced Raman peaks, we have shown that the presence of Pd in NiSi results not only in the retardation of NiSi₂ phase transition to about 900 °C, but also in the redshift ($\sim 3\text{--}4\text{ cm}^{-1}$) of the first-order Raman peaks. The observed Raman frequency downshift with increasing temperature can be described well by a model which has taken into account the contributions of the anharmonic, thermal expansion, and strain effects, revealing the dominant role of the phonon decay. Effects of Pd addition and annealing temperature on the Raman frequency and linewidth have been discussed. The introduction of Pd is found to reduce the Raman frequency downshift, demonstrating the favorable use of NiPdSi for microelectronics applications. © 2009 American Institute of Physics.

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I. INTRODUCTION

Nickel silicide (NiSi) as a potential candidate for future generation of semiconductor devices has attracted much attention in the past decade.^{1,2} Despite of well-recognized advantages of NiSi such as low resistivity, low silicon consumption, and compatibility with germano silicides, there are still some challenges to overcome. On one hand, the agglomeration and transformation of NiSi to high-resistivity NiSi₂ phase at high annealing temperatures seriously limit the silicidation process window. The prominent work of Manginck *et al.*³ that the addition of only 5% of Pt significantly enhances the thermal stability of NiSi has emerged a fertile ground for investigation of the third element addition to NiSi films. By x-ray diffraction measurements and calculations in the frames of the classical nucleation theory,^{3,4} the addition of high-cost Pt, Pd, and Rh (Refs. 4–6) seems to suit perfectly the aims of the stability improvement up to 900 °C up to now. Very recently, a number of reports have also suggested the addition of cheaper metals such as Mo, W, Zr, and Co (Refs. 5, 7, and 8) to NiSi, showing the retardation of NiSi₂ formation, although not as effective as the former alloys, only up to the temperature of 800 °C. Since there is no unambiguous decision on which additive to use, engineers still have to employ the “expensive” ones to satisfy the shrinking dimension demand of microelectronics, where any deviations in process technology could be detrimental. Pd is preferable as it costs four times less than that of Pt (Ref. 9) while it exhibits comparative properties.

On the other hand, thermal degradation issues of microelectronic materials are a dominating concern today and pre-

cise knowledge of the actual surface temperature of silicides especially during device operation is critical for device reliability.¹⁰ The change in vibrational properties in materials with temperature depends strongly on any presence of impurities, alloy elements, and other lattice imperfections. Hence, it appears necessary to analyze the effect of the third element addition to NiSi from both points of view: thermal stability and phonon dynamics. Reconsideration of these two problems is desirable and becomes possible simply by means of one unified, fast, inexpensive, and nondestructive technique: the temperature-dependent Raman spectroscopy. Room-temperature Raman measurements are essential in identifying the temperature of the phase transition, structural peculiarities, and chemical composition, while such fundamental property of the Raman modes as the phonon frequency downshift with temperature evolution indicates the contributions of anharmonicity, thermal expansion, and strain and therefore allows us to judge the device performance at various temperatures.

In this paper we report on a systematic Raman study on NiPdSi film conducted in the range of temperatures 83–563 K and a solid comparison with pure NiSi film. We have demonstrated that this technique is perfectly applicable for both the identification of phase transition temperature and phonon dynamics in NiPdSi. It is verified that the addition of Pd is efficient in retardation in the formation of NiSi₂ up to 900 °C, which provides a significant extension of the silicide process window. We have further shown that the anharmonic effects of phonon decay dominate the Raman frequency downshift with increasing temperature, and as compared to the pure NiSi case, the presence of Pd in NiSi can reduce the Raman frequency downshift for about 4 cm^{-1} , giving an additional evidence of a favorable use of NiPdSi for microelectronics applications.

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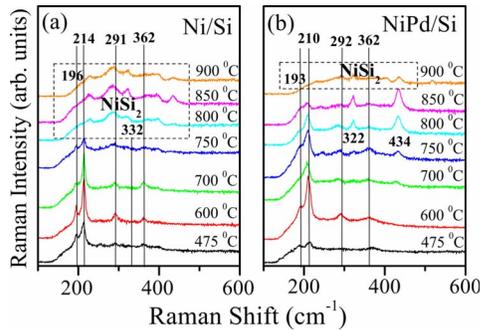


FIG. 1. (Color online) Room-temperature Raman spectra of (a) NiSi and (b) NiPdSi films annealed at various temperatures.

II. EXPERIMENTAL DETAILS

In our experiments Ni with the addition of 10% Pd alloy and for comparison pure Ni films were deposited on *n*-type (111) Si substrate with a resistivity of 10–12 Ω cm by dc magnetron sputtering system. In Ni(*M*) alloy, where *M* indicates any additive metal, the introduction of 5%–10% of metal is considered enough to change the thermal stability of the silicide, although the addition of 10% generally retards the formation of NiSi₂ more effectively.² The silicidation process was carried out in the inert gas ambient in vacuum furnace with the first annealing at 475 °C for 30 min to form Ni(Pd)Si with subsequent etching of the unreacted metal. Annealing temperatures for the second annealing were varied from 600 to 900 °C and also for 30 min. Temperature-dependent Raman measurements were carried out in a back-scattering geometry of $z(x, -)\bar{z}$ on a Jobin Yvon LabRam HR 800 UV micro-Raman system with Andor DU420 CCD detector and a Linkam THMS600 temperature stage using a 514.5 nm line of Ar⁺ laser as an excitation source. The temperature range was chosen from 83 to 563 K with a step of 30 K.

III. ROOM-TEMPERATURE RAMAN MEASUREMENTS

We start from the room-temperature Raman spectra of NiPdSi and for comparison of NiSi films annealed at various temperatures to address the issues of the phase transformation and the thermal stability improvement due to the presence of Pd alloy. Figure 1(a) shows the experimental results for the pure Ni film on Si substrates, which is in good agreement with the earlier reports.^{10–13} NiSi belongs to the orthorhombic structure (MnP-type, space group *Pnma*, D2h16) and 12 Raman active phonons are predicted according to group theory analysis,¹² although only up to eight phonons have been detected in the Raman spectra so far. At 475–750 °C the Raman spectra indicate the formation of NiSi phase. The strongest peak at about 214 cm⁻¹ and weak peaks at 291, 362, and 398 cm⁻¹ are assigned to *A_g* modes.¹² The second strongest peak at 196 cm⁻¹ and another weak one at 255 cm⁻¹ belong to *B_{1g}* and *B_{2g}* phonon modes, respectively.¹² Negligibility of peaks at 255 and 398 cm⁻¹ could be due to the orientation effects in polycrystalline films. Moreover, we do not register the peak at 332 cm⁻¹ [Fig. 1(a)] often found in NiSi films, which we also attribute to the peculiar texture of the film. Further evidence of the

argument is that the Raman peak at 332 cm⁻¹ is attributed to the second predicted phonon mode *B_{1g}*,¹² while the other *B_{1g}* mode at 196 cm⁻¹ is of the low intensity for our samples. From Fig. 1(a) it is obvious that a full transformation to NiSi₂ phase occurs at 800 °C as the first-order Raman peak at 214 cm⁻¹ disappears. All structures corresponding to NiSi₂ phase are found to exhibit diffuse, broad peaks in the range of 200–450 cm⁻¹ (Ref. 13) and no sharp phonon peaks have been observed, although due to the symmetry of the cubic cell (CaF₂-structure) it has one allowed triply degenerate Raman active phonon. These peaks have been assigned to the disorder-induced Raman scattering,¹⁴ which will be discussed later on. Under critical transition condition of 750 °C, besides NiSi peaks at 196 and 214 cm⁻¹, we observe the appearance of diffuse, broad, although not intense peaks, which indicates that NiSi has begun to transform into NiSi₂.

Figure 1(b) displays the room-temperature Raman spectra of NiPd films on Si substrates. At 475 °C the first-order Raman NiSi peak is of a poor intensity. That is mainly due to the Pd impact on the phase formation, similar to Pt addition to NiSi demonstrated in Ref. 2, where metal-rich silicide phases were present on par with NiSi. In the annealing temperature range of 600–850 °C we can observe the presence of NiSi phase with the major Raman peaks at 193, 210, 292, and 362 cm⁻¹ of various intensities. The redshift (~ 3 –4 cm⁻¹) of the peaks at 193 and 210 cm⁻¹ is detected in comparison with the pure NiSi sample in Fig. 1(a). The introduction of Pd increases the interatomic distance, which in turn shifts the vibrational peak positions to lower frequencies. We have attempted to make an approximate estimation of the frequency shift for the first-order peaks in NiPdSi samples from the mass change point of view¹⁵ due to the presence of 10% Pd in Ni film,

$$\omega = \omega_{\text{NiSi}} \sqrt{\frac{\mu_{\text{NiSi}}}{\mu_{\text{NiPdSi}}}}, \quad (1)$$

with ω as the shifted frequency, ω_{NiSi} as the frequency of pure NiSi film, μ_{NiSi} and μ_{NiPdSi} as the effective masses of NiSi and NiPdSi, respectively. Generally, Eq. (1) is valid strictly in the case of a diatomic cubic crystal and could not be directly applied to our samples as the effective mass of a mode is different for various modes. In our estimation we have assumed that in the particular mode the Ni and Pd atoms vibrate in phase against the Si atoms, like in an optic mode of a diatomic cubic crystal, so we could apply the simple effective mass formula in our case, which for example for NiSi is $\mu_{\text{NiSi}} = M_{\text{Ni}}M_{\text{Si}}/(M_{\text{Ni}} + M_{\text{Si}})$, where $M_{\text{Ni,Si}}$ are the atomic masses of the components. Although this is a rough approximation, the values of $\omega = 192.1$ and 209.7 cm⁻¹ can be yielded for the frequency shifts in 196 and 214 cm⁻¹ modes, which are very close to the experimental results. The absence of a significant shift for weaker peaks at 292 and 362 cm⁻¹ needs further investigation.

From Fig. 1(b) it is clear that the addition of Pd in NiSi delays the formation of NiSi₂ phase up to about 900 °C, where the NiSi peaks at 193 and 210 cm⁻¹ disappear, accompanying with the appearance of characteristic NiSi₂ structures. This is the direct experimental evidence for the

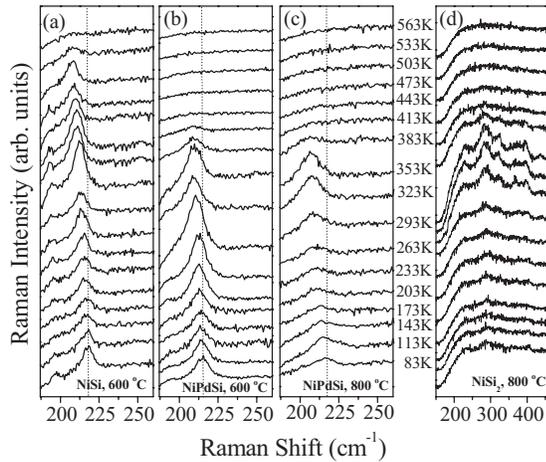


FIG. 2. Temperature-dependent Raman spectra of (a) NiSi and (b) NiPdSi films annealed at 600 °C; (c) NiPdSi and (d) NiSi films at 800 °C.

theoretical predictions in frames of the nucleation theory which used to explain the enhancement of nickel monosilicide stability by the addition of various alloy elements.^{3,4,6} NiSi with the addition of Pd forms a solid state solution $\text{Ni}_{1-x}\text{Pd}_x\text{Si}$. Since the decrease in Gibb's free energy is smaller for $\text{Ni}_{1-x}\text{Pd}_x\text{Si}$ solid solution than that for pure NiSi (for details, please refer to Refs. 3 and 4), we expect the larger activation energy for NiSi_2 nucleation. As a result, a higher formation temperature is needed to achieve NiSi_2 phase in the alloy samples.

In addition, we have noted that another two Raman peaks at 322 and 434 cm^{-1} in NiPdSi spectra gradually become more prominent with the increase in annealing temperature, which have not been reported in the literature before. These two phonon peaks could be attributed to the disorder Raman effects induced by the addition of Pd element. As it is known, the structural disorder in films may arise from contributions of dilute impurities, alloys, vacancies, defect complexes, anharmonicity, as well as from mass variation.¹⁴ In fact, the presence of an alloy introduces the defects to the films, which could lead to the breakage of the translational symmetry, and as a result, the appearance of more peaks in Raman spectra. In comparison, the peaks at similar positions are detected in pure NiSi films when the transformation to NiSi_2 phase is completed [Fig. 1(a), 850 °C], where the disorder-induced Raman scattering arises from the phase transformation (a transformation of the crystal lattice) in the films. It is likely to be assigned to Si-site disorder associated with either or both Ni-antisite defects on Si sites and Si vacancies.¹⁴

IV. TEMPERATURE-DEPENDENT RAMAN MEASUREMENTS

We now focus on systematic investigation of temperature dependencies of the frequencies and damping of the intensities for the strong Raman peaks of NiPdSi ($\omega = 210 \text{ cm}^{-1}$) and NiSi ($\omega = 214 \text{ cm}^{-1}$) annealed at 600 and 800 °C to understand the contribution of Pd addition. Figure 2 shows the temperature-dependent Raman spectra of NiSi, NiPdSi, and NiSi_2 phases initially formed at 600 and 800 °C

in the temperature range of 83–563 K. We have not corrected the Raman spectra for the thermal phonon population factor since we are interested in the Raman peak shift with the temperature, while the thermal factor influences only the Raman peak intensity. In order to accurately determine the Raman frequency of the modes under investigation we use the Lorentz model to fit the Raman peaks throughout the measured temperatures. With the increase in temperature, the Raman spectra clearly indicate a nonlinear decrease in phonon peak position of about 10 cm^{-1} (from 217.8 to 208.0 cm^{-1}) for NiSi [Fig. 2(a)] and of about 6 cm^{-1} (from 215.0 to 209.4 cm^{-1}) for NiPdSi [Fig. 2(b)] annealed at 600 °C. The reduction of $\sim 4 \text{ cm}^{-1}$ in the Raman frequency downshift demonstrates the favorable use of NiPdSi for microelectronics applications. As for NiPdSi formed at 800 °C the peak exhibits a downshift of about 8 cm^{-1} from 216.2 to 207.8 cm^{-1} [Fig. 2(c)], which is also smaller than that in pure NiSi film. In contrast, the temperature-dependent Raman peaks of NiSi_2 do not show any significant change [Fig. 2(d)], which could be due to a combined effect of lattice anharmonicity and structural disorder.¹⁶ The change in the phonon density of states with temperature for these modes has been compensated by the activation of lattice disorder.

We can quantitatively analyze the experimental peak downshift for NiPdSi and NiSi. The downshift in the Raman frequency with the increase in temperature is mainly due to the effects of the anharmonic coupling to other phonons, thermal expansion, and lattice-mismatch-induced strain between thin films and substrates. In modeling the Raman shift, the temperature-dependent Raman frequency $\omega(T)$ due to various factors can be written as^{10,17}

$$\omega(T) = \omega_0 + \Delta\omega_d(T) + \Delta\omega_e(T) + \Delta\omega_s(T), \quad (2)$$

with ω_0 as the perfect harmonic lattice phonon frequency of the optical mode, $\Delta\omega_d(T)$ as the contribution of the anharmonic coupling to phonons of other branches, $\Delta\omega_e(T)$ as the one from thermal expansion of the lattice or volume change, and $\Delta\omega_s(T)$ as the thermal mismatch between the silicide film and the silicon substrate. $\Delta\omega_d(T)$ can be described by

$$\Delta\omega_d(T) = A \left[1 + \frac{2}{\exp\left(\frac{\hbar\omega_0}{2kT}\right) - 1} \right] + B \left[1 + \frac{3}{\exp\left(\frac{\hbar\omega_0}{3kT}\right) - 1} + \frac{3}{\left[\exp\left(\frac{\hbar\omega_0}{3kT}\right) - 1\right]^2} \right], \quad (3)$$

where the first term is the decay of zero-center phonons into two phonons (three-phonon coupling) and the second one represents the decay into three phonons (four-phonon coupling). A and B are the anharmonic constants, which are selected as fitting parameters. We have considered the symmetric decays of zone-center phonons into two and three phonons with frequencies $\omega_0/2$ and $\omega_0/3$, respectively.

The term $\Delta\omega_e(T)$ could be given as

$$\Delta\omega_e(T) = \omega_0 \left\{ \exp \left[-\gamma_g \int_0^T [\alpha_a(\tilde{T}) + \alpha_b(\tilde{T}) + \alpha_c(\tilde{T})] d\tilde{T} \right] - 1 \right\}. \quad (4)$$

The updated experimental information on thermal coefficients of linear expansion $\alpha_i(\tilde{T})$, where $i=a, b, c$ for NiSi in Ref. 18, has established the base for evaluation of contribution of thermal expansion to anharmonicity. The values of $\alpha_a=21.5+0.0334(T-T_0)$ (10^{-6} K^{-1}), $\alpha_b=-16.1+0.0459(T-T_0)$ (10^{-6} K^{-1}), and $\alpha_c=25.3+0.0207(T-T_0)$ (10^{-6} K^{-1}), where $T_0=298 \text{ K}$, are taken for both kinds of samples. As there are no published values of Grüneisen constant γ_g for NiSi and NiPdSi films we adopt the value $\gamma_g=0.98$ for crystalline Si (Ref. 19) in our calculations.

There is a noticeable lattice and thermal mismatches between Ni(Pd)Si and Si, which could result in the strain-induced contribution $\Delta\omega_s(T)$ to the phonon frequency shift. The different thermal expansion coefficients of a thin film and a substrate lead to a temperature-dependent in-plane strain $\varepsilon(T)$,¹⁷

$$\varepsilon(T) = (1 + \varepsilon_g) \frac{1 + \int_{T_s}^T \alpha_{a,s}(\tilde{T}) d\tilde{T}}{1 + \int_{T_s}^T [\alpha_i(\tilde{T}) + \alpha_j(\tilde{T})] d\tilde{T}} - 1, \quad (5)$$

where $\alpha_{a,s}$ and α_i, α_j ($i=a, b, c; j=b, c, a$) are the temperature-dependent in-plane linear expansion coefficients of the substrate and film, respectively, and ε_g is the residual strain in silicide film at silicidation temperature T_s , which is assumed to be zero as in Ref. 20. Since the phonon deformation potentials and elastic constants of the nickel monosilicide films are not available up to now, we set them as one unified constant C , which is a fitting parameter in our calculations. Therefore, the strain-induced contribution $\Delta\omega_s(T)$ to the Raman shift of the frequency is

$$\Delta\omega_s(T) = C\varepsilon(T). \quad (6)$$

In Fig. 3, we display the fitting results for the experimental Raman frequencies of the strongest phonon peak in NiSi and NiPdSi (solid curves). They are decomposed into the contributions of $\Delta\omega_d(T)$, $\Delta\omega_e(T)$, and $\Delta\omega_s(T)$, leading to the downshift in the phonon frequency with increasing temperature. We note that the present model describes well the downshift in the phonon frequency, yielding the reasonable value of $C=7.0 \text{ cm}^{-1}$, together with the results of A, B , and ω_0 listed in Fig. 3. From the ratio of A/B we can conclude the mechanism of the zone-center optical phonon decay into the lower energy phonons to be mainly a three-phonon process for pure NiSi and NiPdSi annealed at 800 °C, as it equals to 115.0 and 24.9, respectively. For NiPdSi annealed at 600 °C the ratio of A/B is much smaller (≈ 1.6), indicating the possibility of both three-phonon and four-phonon decay processes. It is due to the incomplete formation of solid solution $\text{Ni}_{1-x}\text{Pd}_x\text{Si}$ at 600 °C and the consequent compositional disorder in the films that results in the possibility of both mechanisms of phonon decay. At 800 °C the composi-

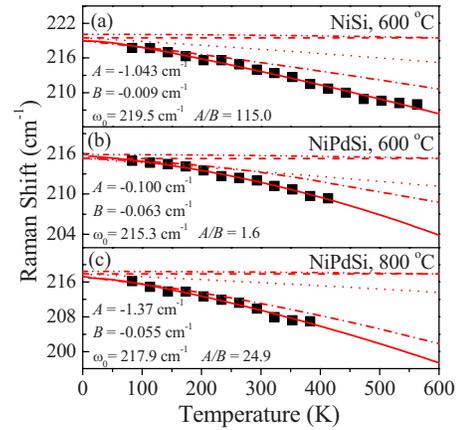


FIG. 3. (Color online) Temperature dependence of Raman peak positions in (a) NiSi formed at 600 °C, (b) NiPdSi films formed at 600 °C, and (c) NiPdSi films formed at 800 °C. The solid squares are the experimental data. The solid curves represent the least-square theoretical fit involving all the contributions from Eq. (2). The contributions from the different terms in Eq. (2) are also displayed separately, where ω_0 : dashed curves, $\omega_0 + \Delta\omega_d$: dashed-dotted curves, $\omega_0 + \Delta\omega_e$: dotted curves, and $\omega_0 + \Delta\omega_s$: dashed-dot-dotted curves.

tion of the NiPdSi film becomes more homogenous leading to the prevailing three-phonon process decay.

We can also clearly observe the variation in harmonic frequency in NiSi films by the addition of 10% Pd, which can be attributed well to the change in the lattice constant. For the NiPdSi samples at 600 °C due to the incorporation of Pd diffusing interstitially in the film during silicidation process, the lattice constant increases, corresponding to the decrease in ω_0 . At higher temperatures, when Pd is incorporated substitutionally on the Ni sublattice with the formation of $\text{Ni}_{0.9}\text{Pd}_{0.1}\text{Si}$ solid solution the lattice constant decreases slightly, resulting in the increase in ω_0 . From the analysis of fitting results $\Delta\omega_s(T)$ in Fig. 3 we further notice that the lattice and thermal mismatch-induced strain are small and seem not to affect the Raman frequency downshift for all samples. It was assumed in Ref. 10 that the phonon decay process is a dominant process to contribute to the Raman frequency downshift in pure NiSi films (the impact of the thermal expansion and strain-induced lattice mismatch has not been considered at that time). Performing the full contribution to the Raman frequency in Fig. 3, we confirm that the phonon decay $\Delta\omega_d(T)$ has the major impact on frequency downshift for NiSi and NiPdSi films with the minor role of thermal expansion $\Delta\omega_e(T)$.

Finally, in addition to the Raman frequency shift, the variation in the linewidth of the Raman peaks with the increase in temperature is worthy of being considered since it represents the phonon lifetimes. We have observed no significant change in the width of NiSi peaks for NiSi and NiPdSi samples for temperatures higher than 233 K. However, there is a nonlinear increase in a linewidth in the temperature range of 83–233 K. The linewidth is about 5–6 cm^{-1} smaller for pure NiSi and 2 cm^{-1} broader for NiPdSi annealed at 800 °C than that in NiPdSi film annealed at 600 °C. There are two main mechanisms controlling the linewidth in most materials: the anharmonic phonon decay into other phonons and the phonon scattering at impurities,

defect centers, lattice imperfections, or alloy elements that leads to inhomogeneous broadening of the linewidth. It is widely recognized that the addition of impurity atoms will impact the lattice structure of the film, and the linewidth of Raman peaks will change consequently, which we observe in the case of NiPdSi annealed at 600 °C, while the total frequency downshift is 4 cm⁻¹ less than for pure NiSi film, indicating the smaller contribution of anharmonicity from the decay process.

The broadest linewidth for NiPdSi annealed at 800 °C in combination with almost the same frequency downshift as in pure NiSi is obviously influenced by both anharmonic phonon decay into other phonons and phonon scattering on Pd atoms. In this case the higher annealing temperature gives rise to the prevailing three-phonon anharmonic decay process despite the presence of Pd, yielding the “double” impact on the linewidth broadening.

V. CONCLUSIONS

In summary, we have reported a detailed investigation on the characteristics of Raman scattering in NiSi and NiPdSi films annealed at various temperatures. The enhancement of thermal stability, the redshift in the first-order Raman peak at 214–210 cm⁻¹, and the appearance of vibrational modes at 322 and 434 cm⁻¹ in NiPdSi spectra at higher temperatures are attributed to the presence of Pd and alloy disorder-induced effects, respectively. The observed downshift in the Raman frequency from the temperature-dependent micro-Raman spectra was modeled theoretically taking into account the phonon decay, thermal expansion, and thermal and lattice mismatch-induced strains between the film and the substrate. It has yielded the key role of the phonon decay into other phonons with the minor addition of thermal expansion on the Raman frequency downshift. The evidence of a favorable use of NiPdSi for microelectronics applications has been presented by the fact that the introduction of Pd in NiSi can reduce the Raman frequency downshift for about 4 cm⁻¹. The weight of the three-phonon and four-phonon contributions to the total phonon decay is found to be influenced by both the composition of the film and annealing temperature.

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