Penetration depth at various Raman excitation wavelengths and stress model for Raman spectrum in biaxially-strained Si

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The carrier mobility of Si material can be enhanced under strain, and the stress magnitude can be measured by the Raman spectrum. In this paper, we aim to study the penetration depths into biaxially-strained Si materials at various Raman excitation wavelengths and the stress model corresponding to Raman spectrum in biaxially-strained Si. The experimental results show that it is best to use 325 nm excitation to measure the material stress in the top strained Si layer, and that one must pay attention to the distortion of the buffer layers on measuring results while 514 nm excitation is also measurable. Moreover, we established the stress model for Raman spectrum of biaxially-strained Si based on the Secular equation. One can obtain the stress magnitude in biaxially-strained Si by the model, as long as the results of the Raman spectrum are given. Our quantitative results can provide valuable references for stress analysis on strained materials.

strained Si, Raman, stress, model

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1   Introduction

The carrier mobility of Si materials can be enhanced significantly under strain, which has been widely applied in the performance improvement of CMOS and circuits [1–3]. The stress magnitude of strained materials can be examined by Raman scattering measurements [4,5]. It is the most important one of the characterization techniques of strained materials. However, there still have some problems about stress measurement of the Raman spectrum that need to be studied, mainly in the two following aspects.

The optical penetration depths into strained materials are closely related to the Raman excitation wavelengths. Generally, biaxially-strained Si materials are prepared by a buffer layer technique. Various buffer layers are firstly grown on an Si substrate until the relaxed $Si_{1-x}Ge_x$ layer is obtained. Next, the strained Si epitaxial layer desired is deposited. So, the reasonable Raman excitation wavelength must be chosen when the stress magnitude of biaxially-strained Si materials is measured by the Raman spectrum. If an unreasonable wavelength is chosen, distortion of the buffer layers on measuring results will occur, and no desired results are obtained, when the penetration depth into sample materials is beyond the thickness of the strained Si epitaxial layer. Although literatures [6,7] have listed the theoretical results for the penetration depth into the strained Si material versus various Raman excitation wavelengths (Table 1), we still need to evaluate the specific measurement effects by using various Raman excitation wavelengths.

On the other hand, the Raman shifts, not the stress magnitude are shown in the figures. In order to obtain the infor-

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Table 1 Relationship between Raman excitation wavelengths and penetration depths

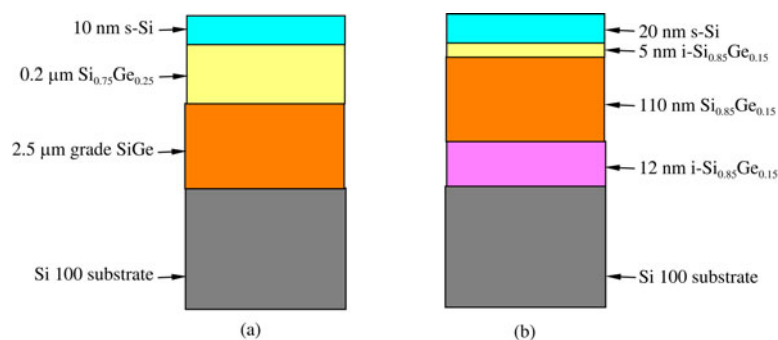| Wavelength (nm)	Energy (eV)	Depth (nm)
514.5	2.41	300
457.9	2.79	65
413.1	3.00	12
351.0	3.53	5

mation for stress magnitude, the Raman shifts in the pictures need a conversion process. Namely, we must establish the theoretical relationship between the Raman spectrum and the stress magnitude. Note that, the stress magnitude of strained Si materials is also close to the orientation of the relaxed $Si_{1-x}Ge_x$ substrate. As far as can be determined, the literatures have only reported the stress model of the Raman spectrum for biaxially-strained Si (001) [8,9]. At the same time, the derivation is too simplified to understand.

In view of these factors, our attention focused on the optical penetration depths into biaxially-strained Si materials using various Raman excitation wavelengths and the effect of buffer layer on Raman stress measurement. Moreover, we will obtain the theoretical relationship between the Raman spectrum and stress magnitude in (001), (101) and (111) biaxially-strained Si materials on the basis of the Secular equation and the Raman selection rules. Our conclusions in this paper can provide valuable references for stress measurement and analysis of strain materials.

2 Penetration depth experiments

2.1 Experimental procedure

Two kinds of strained Si material samples with different

structure were prepared by RPCVD (Figure 1). The fabrication procedure for sample A is: (i) deposit gradient $Si_{1-x}Ge_x$ layers with the thickness of 2.5 μm on an Si (100) substrate; (ii) form a relaxed $Si_{0.75}Ge_{0.25}$ layer on gradient $Si_{1-x}Ge_x$ layers with the thickness of 0.2 μm; 3) epitaxy strained Si film on a relaxed $Si_{0.75}Ge_{0.25}$ layer with thickness of 10 nm. The structure of c is different from sample A. Its structure contains the Si (100) substrate, 12 nm intrinsic $Si_{0.85}Ge_{0.15}$ layer, 110 nm doped $Si_{0.85}Ge_{0.15}$ layer, 5 nm intrinsic $Si_{0.85}Ge_{0.15}$ layer and 20 nm strained Si film in turn.

Raman scattering measurements of samples A and B were performed using two different spectrometers. Their experimental conditions are listed in Table 2.

2.2 Experimental results and discussion

Raman spectrum of sample A with a 514 nm excitation is shown in Figure 2(a). As can be seen, peak 515.47 (corresponding to strained Si layer) and peak 507.1 (corresponding to $Si_{0.75}Ge_{0.25}$ layer) are found. Additionally, the intensity of peak 507.1 is significantly higher than the one of peak 515.47. This indicates that the penetration depth at 514 nm excitation reaches to the relaxed $Si_{0.75}Ge_{0.25}$ layer shown in Figure 1(a). Results from Figure 2(b) show that peak 514 appears conspicuously (corresponding to the strained Si layer). This indicates that the optical penetration depth at 325 nm excitation did not pass through the strained Si layer of Figure 1(a).

In order to further study the penetration depth at various Raman excitation wavelengths in strained Si materials, we also measure sample B under the same conditions (Figures 3(a) and (b)). Peak 519 with high intensity and superimposed peak 515.7 are found in Figure 3(a). This indicates that the penetration depth at 514 nm excitation reaches to the Si substrate area in Figure 1(b). Only peak 516 (corre-

Figure 1 (Color online) strained Si material samples with different structure. (a) Sample A; (b) sample B.

Table 2 Experimental condition of Raman scattering measurements

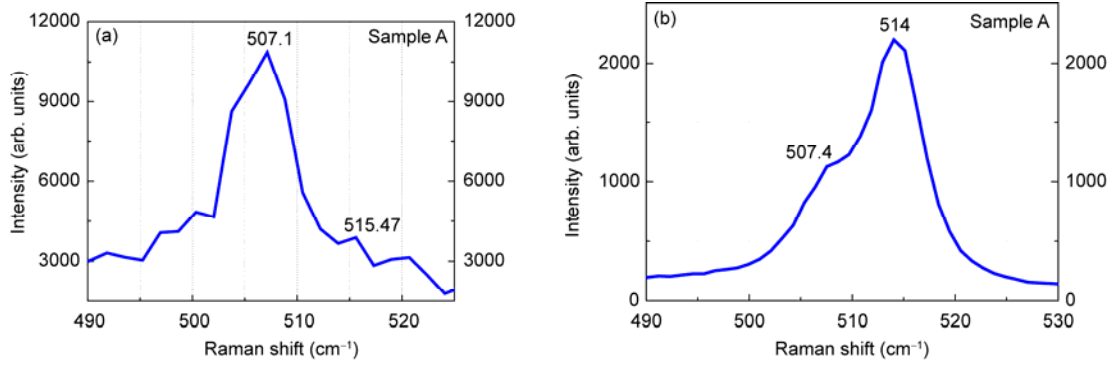| Wavelength (nm)	Name of Raman spectrometer	Sample temperature	Laser power (mV)	Magnification of objective lens	Numerical aperture
514.5	Renishaw inVia	Room temperature	30 mW	50×	0.9
325.0	Kimmon IK 3301R-G	Room temperature	0.5 mW	40×	0.5

Figure 2   (Color online) (a) Raman spectrum of sample A using 514 nm excitation. (b) Raman spectrum of sample A using 325 nm excitation.
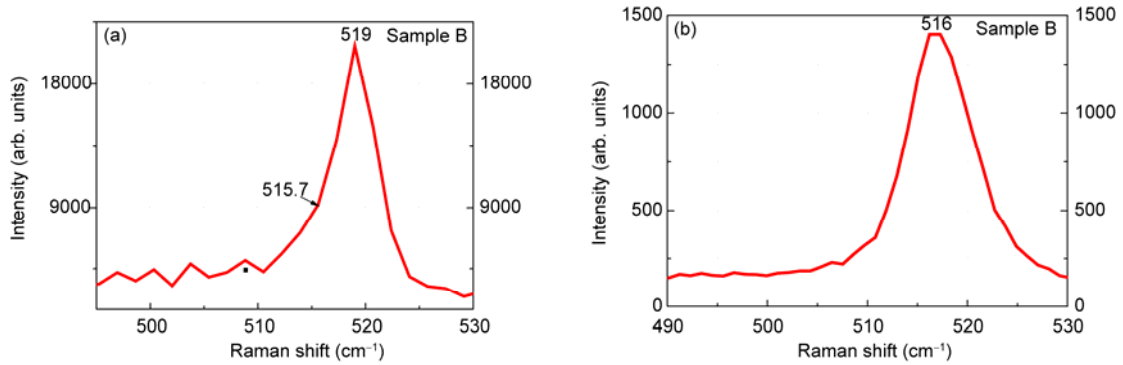

Figure 3   (Color online) (a) Raman spectrum of sample B using 514 nm excitation. (b) Raman spectrum of sample B using 325 nm excitation.

sponding to strained Si layer) appears in Figure 3(b) when a 325 nm excitation is used. This indicates that the penetration depth at 325 nm excitation did not pass through the strained Si layer in Figure 1(b).

Contrasting with the structure parameters in Figure 1, our measurement results are consistent with the theoretical results from Table 1. Being that the penetration depths are on the order of a few nanometers and a few hundred nanometers in strained materials when using 325 nm and 514 nm excitation, respectively. Notably, the Raman spectrums of samples A and B can be obtained by using a 514 nm excitation, but the signals are very weak. Assuming that the content of the buffer layer material is too large, meaning its corresponding signals is much stronger, our desired signals will be annihilated. Therefore, it is best to use a 325 nm excitation to measure the magnitude of stress in the top strained Si layer, and one must pay attention to the distortion of the buffer layers on measuring results while a 514 nm excitation is also measurable.

3   Theoretical Raman stress model

3.1   Secular equation and selection rules

Atomic separations in strained materials are different from those of unstrained ones. This difference between strained and unstrained materials is in contrast with the Raman frequency shift. That is the foundational principle of Raman stress measurement. The Raman characteristic spectrum (ω_0) of unstrained Si material is about 520 cm^{-1}. The frequency will shift when stress is applied to unstrained Si material. The magnitude of shifting $\Delta\omega$ has the following relationship

$$\Delta\omega = \omega - \omega_0 \approx \frac{\lambda}{2\omega_0}, \tag{1}$$

where ω is the Raman wave number of strained Si, and λ is the eigenvalues of the Secular equation for Si based diamond-like materials [10,11]

$$\begin{vmatrix} p\varepsilon_{xx} + q(\varepsilon_{yy}+\varepsilon_{zz}) - \lambda & 2r\varepsilon_{xy} & 2r\varepsilon_{zx} \\ 2r\varepsilon_{xy} & p\varepsilon_{yy} + q(\varepsilon_{xx}+\varepsilon_{zz}) - \lambda & 2r\varepsilon_{yz} \\ 2r\varepsilon_{zx} & 2r\varepsilon_{yz} & p\varepsilon_{zz} + q(\varepsilon_{yy}+\varepsilon_{xx}) - \lambda \end{vmatrix} = 0, \tag{2}$$

where ε_{ij} is strain tensors component, and p, q, r are the coefficients of the photonic material with values of −1.85, −2.32, and −0.71, respectively.

As shown in eq. (1), there exists a relationship between $\Delta\omega$ measured by the Raman spectrum and the eigenvalues

λ as a function of the strain tensor ε_{ij} (corresponding to material stress). Therefore, we can present the magnitudes of stress in different strained materials as long as $\Delta\omega$ is measured by Raman spectrum and λ is obtained by solving Secular equations. Notably, the Secular equation is a 3×3 determinant and the number of its eigenvalues is one, two, or three. This means that there exist at most three Raman characteristic peaks for strained materials. In order to explain this problem, we will introduce the Raman selection rules in details.

The scattering efficiency of the Raman spectrum I is determined by the following equation

$$I = C\sum_j \left| e_i \cdot R_j \cdot e_s \right|^2, \tag{3}$$

where C is a constant, e_i and e_s are the polarization directions of incident and scattered light respectively, and R_j is the materials' Raman tensor. According to ref. [12], there are three Raman tensors in Si material. In the lattice coordinate system, i.e. x is [100] direction, y is [010] direction, z is [001] direction.

$$R_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}, \quad R_2 = \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \quad R_3 = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{4}$$

where d is a non-zero element.

As can be seen from eq. (3), various vibration modes of optical phonon will be observed (i.e., the scattering efficiency is non-zero) by selecting the appropriate directions of the incident polarized light and scattered light. Each vibration mode has its corresponding eigenvalue λ. These are the so-called Raman selection rules. According to eq. (3), the Raman selection rules of strained Si materials are specified in Table 3 below ($\sqrt{}$ represents some mode is effective).

Table 3 Backscattering selection rules of (001), (101), and (111) strained Si materials

Polarization directions		Vibration modes		
e_i	e_s	R_1	R_2	R_3
(001) backscattering				
[100]	[100]	–	–	–
[100]	[010]	–	–	$\sqrt{}$
[1-10]	[1-10]	–	–	$\sqrt{}$
[110]	[1-10]	–	–	–
(101) backscattering				
[10-1]	[10-1]	–	$\sqrt{}$	–
[10-1]	[010]	$\sqrt{}$	–	$\sqrt{}$
[010]	[010]	–	–	–
(111) backscattering				
[11-2]	[11-2]	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$
[1-10]	[11-2]	$\sqrt{}$	$\sqrt{}$	–
[1-10]	[1-10]	–	–	$\sqrt{}$

3.2 Raman stress model

As can be seen from eq. (2), the eigenvalue λ of the Secular equation is a function of the strain tensor. So, to obtain the theoretical relationship of the Raman frequency shift and stress, the strain tensor of strained Si materials must firstly be calculated. Based on the principle of strain tensor and the generalized Hook laws, the strain tensors of biaxially strained Si materials grown on a typical plain are obtained in this paper. Two points about the solving procedure need to be emphasized. First, one needs pay attention to the coordinate transformation between the sample coordinate system and crystal cell coordinate system during the solution procedure (Figure 4).

Strain tensor in (001) biaxially strained Si is as follows.

$$\varepsilon_{xx} = \frac{c_{11}+c_{12}}{2c_{11}c_{12}+c_{11}^2}T, \quad \varepsilon_{yy} = \frac{c_{11}+c_{12}}{2c_{11}c_{12}+c_{11}^2}T,$$
$$\varepsilon_{zz} = \frac{-c_{12}}{2c_{11}c_{12}+c_{11}^2}T, \quad \varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz} = 0. \tag{5}$$

Strain tensor in (101) biaxially strained Si,

$$\varepsilon_{xx} = \varepsilon_{zz} = \frac{c_{11}-2c_{12}}{2c_{11}^2+2c_{11}c_{12}-4c_{12}^2}T,$$
$$\varepsilon_{yy} = \frac{c_{11}}{c_{11}^2+c_{11}c_{12}-2c_{12}^2}T,$$
$$\varepsilon_{xz} = -\frac{1}{2c_{44}}T, \quad \varepsilon_{xy} = \varepsilon_{yz} = 0. \tag{6}$$

Strain tensor in (111) biaxially strained Si,

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \frac{2}{3(c_{11}+2c_{12})}T,$$
$$\varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz} = -\frac{1}{3c_{44}}T. \tag{7}$$

Substituting the strain tensors in eqs. (5)–(7) into the eigenvalue λ obtained by solving the Secular equation, we
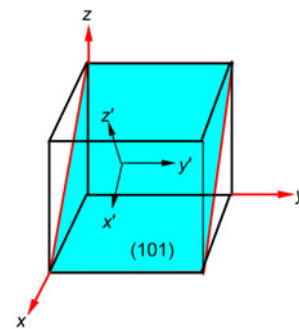

Figure 4 (Color online) Sample coordinate system and crystal cell coordinate system.

establish the stress model for the Raman spectrum of biaxially-strained Si eventually. Notably, only the R_3 vibration mode can be observed for biaxially-strained Si (001) according to selection rule in Table 2 and we need only obtain the eigenvalue λ_3 from the Secular equation. For (101) strained Si, the case is complex. If both the incident direction and the scattering direction are [10–1], only mode R_2 can be observed. If the incident direction is [10–1] and the scattering direction is [010], R_1 and R_3 will be selected. If both the incident and the scattering directions are [010], no mode occurs. This means that all of the eigenvalues need to be calculated for (101) strained Si materials. The case of (111) strained Si materials is similar with (101) strained Si materials. If both the incident and the scattering directions are [11–2], all of three vibration modes are selected. Moreover, since the two transverse phonons' vibration mode overlaps, there are only two different eigenvalues for biaxially strained Si (111) material. If the incident direction is [1–10] and the scattering direction is [11–2], the two transverse mode are selected. If both the incident and the scattering directions are [1–10], only the longitudinal phonon mode can be observed.

All the eigenvalues of the Secular equation for (001), (101) and (111) biaxially strained Si materials are given in the following.

$$\begin{cases} \lambda_{1,2} = p\varepsilon_{xx} + q(\varepsilon_{xx} + \varepsilon_{zz}), \\ \lambda_3 = p\varepsilon_{zz} + 2q\varepsilon_{xx}, \end{cases}$$

$$\begin{cases} \lambda_1 = p\varepsilon_{yy} + 2q\varepsilon_{xx}, \\ \lambda_2 = p\varepsilon_{xx} + q(\varepsilon_{xx} + \varepsilon_{yy}) + 2r\varepsilon_{xz}, \\ \lambda_3 = p\varepsilon_{xx} + q(\varepsilon_{xx} + \varepsilon_{yy}) - 2r\varepsilon_{xz}, \end{cases}$$

$$\begin{cases} \lambda_{1,2} = (p + 2q)\varepsilon_{xx} - 2r\varepsilon_{xy}, \\ \lambda_3 = (p + 2q)\varepsilon_{xx} + 4r\varepsilon_{xy}, \end{cases}$$

Based on the principle above, substituting eqs. (5)–(7) and related parameters into the eigenvalues we needed, the theoretical relationship between the Raman frequency shift and stress are established respectively in (001), (101) and (111) biaxially strained Si materials. (001) strained material is $\Delta\omega_3 = -5.072802 24929709T$, (101) strained material are $\Delta\omega_1 = -3.46298766929452T$, $\Delta\omega_2 = -1.71550743826406T$, and $\Delta\omega_3 = -6.38301691993283T$, (111) material are $\Delta\omega_{1,2} = -5.409673 83638673T$, and $\Delta\omega_3 = -0.74216435471795T$.

The function relationship curves between the Raman frequency shift $\Delta\omega$ and stress T in (001), (101), and (111) biaxially strained Si materials are shown in Figure 5. As can be seen, the frequency shift $\Delta\omega$ is about −5.073 cm^{-1} for (001) biaxially strained Si under 1 GPa. This result is consistent with the experimental results in the literatures. For other biaxially strained Si, the measurement results by Raman spectrum can be transformed to their corresponding stresses based on Figure 5.

4   Conclusions

In this paper, the penetration depths at various Raman excitation wavelengths and the corresponding stress model to the Raman spectrum in biaxially-strained Si are studied. The experimental results show that the penetration depths at excitations of 325 nm and 514 nm are about a few nanometers and a few hundred nanometers respectively in strained materials. Also, a 325 nm excitation is the optimal option to measure the magnitude of stress in the top strained Si layer, and one must pay attention to the distortion of the buffer layers on measurment results while a 514 nm excitation is also measurable.

Additionally, based on the principle of strain tensor and the generalized Hook laws, the strain tensors of biaxially strained Si materials grown on a typical plain are obtained,
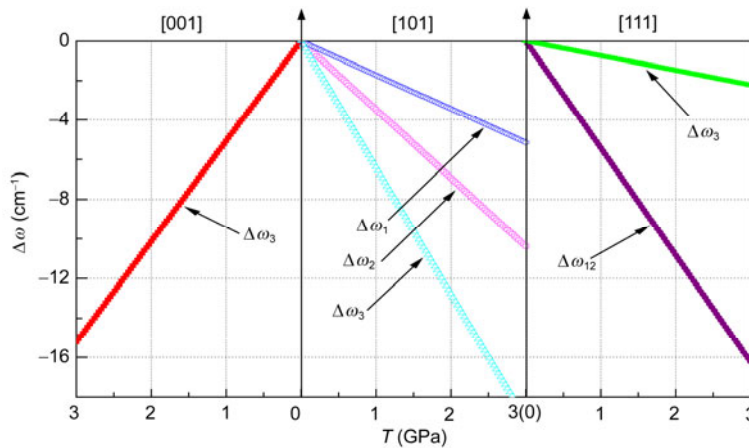

Figure 5   (Color online) Stress model for Raman spectrum in biaxially-strained Si.

and the theoretical relationship between Raman frequency shift and stress is established from the Secular equation respectively in (001), (101) and (111) biaxially strained Si materials. One can obtain the stress magnitude in biaxially-strained Si by the model, as long as the results of Raman spectrum are given. Our quantitative results can provide valuable references to stress analysis on strained materials.

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