Resonance Raman spectroscopy of silicene and germanene

G. Kukucska
Department of Biological Physics, Eötvös Loránd University, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary

V. Zólyomi
School of Physics and Astronomy, University of Manchester, Oxford Road, Manchester M13 9PL, UK

J. Koltai
Department of Biological Physics, Eötvös Loránd University, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary
E-mail: koltai@elte.hu

August 2018

Abstract. We present a third-nearest neighbour tight-binding model parametrized from first principles density functional theory and use it to describe Raman processes involving scattering of quasiparticles by, either, two phonons, or, one phonon and one point defect. We demonstrate that in silicene, the second lowest conduction band at the M point introduces a second plasmon energy at 2.77 eV previously not described in the literature that gives rise to an additional resonance at the corresponding laser excitation energy, measurably higher than the one originating from the first plasmon energy at 2.12 eV. We show that in germanene, spin-orbit coupling splits a fourfold degenerate state at the Γ point in the valence band into two Kramers doublets by 196 meV, and needs to be taken into account for the correct description of resonant Raman scattering in this material, as opposed to silicene where this effect is much smaller and can be safely neglected. We use our model to predict scattering cross sections for defect induced scattering involving adatoms, substitutional impurities, Stone-Wales pairs, and vacancies, and argue that the presence of each of these defects in silicene and germanene can be matched to specific features in the Raman response.

Keywords: Resonance Raman, silicene, germanene, DFT, SOC

1. Introduction

Graphene-like hexagonal materials composed of silicon or germanium are unique two-dimensional (2D) crystals with a promising future in nanoelectronics. These structures
Resonance Raman spectroscopy of silicene and germanene

Figure 1. Structure of silicene and germanene

were predicted to be stable by density functional theory (11, 2), and fabricated on metallic substrates amid intensive experimental pursuit over the past decade (3–11). While synthesis of free-standing monolayers is still not accomplished, recent studies have shown that both silicene (12) and germanene (13) monolayers synthesized on metallic surfaces exhibit Dirac-like bands. Moreover, these hybrid structures were already used to fabricate transistors from both silicene (14) and germanene (15).

What sets silicene and germanene apart from their carbon counterpart (16) is that these structures exhibit a sublattice buckling, that is, the A and B sublattices of the honeycomb structure are vertically shifted relative to one another as shown in Fig. 1. The buckled structure introduces new physics such as the opening of a spin-orbit induced band gap of 1–2 meV and 24 meV in silicene and germanene, respectively (17–21). Moreover, a topological phase transition can be induced in such materials by applying a perpendicular electric field which introduces a tuneable band gap up to \( \sim 100 \text{ meV} \) (18, 22).

Raman spectroscopy offers a powerful way to analyse electronic and vibrational properties of these materials. This non-destructive technique relies on inelastic scattering of light to probe the phononic excitations in the lattice. It is also well suited to probe quantitative and qualitative properties of perturbations such as strain (23, 24), doping (24, 25) or lattice defects (26). Defect scattering can activate otherwise forbidden peaks in the spectra, which can be used to identify the type of defect or edge orientation (27–29). Intensity of these peaks can be calculated within fourth-order time-dependent perturbation theory. These fourth-order processes also include scattering of defect-free systems by emission of two phonons.

In this paper, we present a tight-binding (TB) model parametrised directly from first principles density functional theory (DFT) to calculate i) two-phonon and ii) defect induced single-phonon Raman processes in freestanding monolayer silicene and germanene. We evaluate defect scattering matrix elements within the tight-binding formalism for various defects, and use these matrix elements to calculate the Raman
spectra for defect induced processes. We argue, that the position and relative intensity ratio of the dominant peaks can be used to distinguish between different types of defects, implying that Raman characterization can be used to indicate the concentration of different point defects in silicene and germanene.

We demonstrate that in germanene spin-orbit coupling must be taken into account for an accurate description of excitations, whereas in silicene it can be safely neglected. We also compare our model for two-phonon processes to a previously developed non-orthogonal TB model \cite{30} of graphene and silicene, and point out a dependence of the predictions on the sublattice buckling parameter. In particular, by calculating the two phonon Raman spectra of germanene and comparing these spectra to the two phonon spectra of graphene we demonstrate a connection between the sublattice buckling and the amplitude of Raman peaks originating from out-of-plane vibrations.

2. Methods

2.1. Raman intensities

We compute the Raman cross sections within the established fourth order time-dependent perturbation theory \cite{29,31,33}. The scattering amplitudes ($K$) of the eight relevant Feynman diagrams \cite{29} as presented in Fig. 2 for two-phonon (pp) and in Fig. 3 defect induced (pd) diagrams can be written in the general form

$$K_{pp}^{\mu,\nu} = \sum_{A,B,C} \frac{M_{JC}^{e-p} M_{CB}^{e-ph,\mu} M_{BA}^{e-ph,\nu} M_{Ai}^{e-p}}{(E_i - E_C)(E_i - E_B)(E_i - E_A)},$$

(1)
Resonance Raman spectroscopy of silicene and germanene

|          | \(a_{\text{Si}}\) | \(\Delta_{\text{Si}}\) | \(a_{\text{Ge}}\) | \(\Delta_{\text{Ge}}\) |
|----------|-----------------|-----------------|-----------------|-----------------|
| LDA      | 3.825 Å         | 0.439 Å         | 3.968 Å         | 0.647 Å         |
| HSE06    | 3.841 Å         | 0.434 Å         | 3.989 Å         | 0.645 Å         |

Table 1. Structural parameters of silicene and germanene

\[
K_{pd}^\mu = \sum_{A,B,C} M_{fC}^{e-p} M_{CB}^{e-ph,\mu} M_{BA}^{d} M_{Ai}^{e-p} \frac{1}{(E_i - E_C)(E_i - E_B)(E_i - E_A)},
\]

where \(\mu, \nu\) are phonon branch indices, \(i, f\) denote the initial and final state of the system, respectively, \(A, B, C\) are virtual intermediate states, \(E_i, E_A, E_B, E_C, E_f\) denote the sum of the energies of all quasiparticles present in these states, and \(M_{fC}^{e-p}, M_{CB}^{e-ph,\mu}, M_{BA}^{d}\) are the electron-photon, electron-phonon, and defect scattering matrix elements, respectively. The Raman cross section \(I\) can be calculated directly from these amplitudes by summing over all possible final states, and can be expressed as

\[
I_{pp}(\omega) = \sum_{f,\mu\nu} |K_{pp}^{\mu,\nu}|^2 \delta(\omega_\mu + \omega_\nu - \omega)(n(\omega_\mu) + 1)(n(\omega_\nu) + 1),
\]

\[
I_{pd}(\omega) = \sum_{f,\mu} |K_{pd}^{\mu}|^2 \delta(\omega_\mu - \omega)(n(\omega_\mu) + 1),
\]

where \(\delta(x)\) is the Dirac delta function ensuring the conservation of energy between the initial and final state, \(\omega\) is the Raman shift and \(n(\omega_\mu)\) is the Bose-Einstein distribution due to the induced emission of a phonon with frequency \(\omega_\mu\). These matrix elements determine the amplitude of possible allowed and forbidden transitions. Their accurate description is essential in order to obtain correct peak intensities. In our model the matrix elements are calculated within the tight-binding approximation as presented below in Section 2.4.

Another important factor in calculating the Raman intensities is the resonance behaviour arising from the energy denominators. When the energy of a virtual state is close to the initial or final state energy, the corresponding energy denominator will become nearly zero, which increases the intensity dramatically. It is possible for two of the energy denominators to be simultaneously nearly zero, which is called double resonance, and can result in even larger intensities compared to the single resonant processes. However, if one of the denominators in Eqs. 1 and 2 becomes zero, the transmission amplitudes will diverge resulting in infinite peak intensities. In order to avoid these singularities numerically an imaginary component is introduced in the energy denominators, which in a physical sense relate directly to the finite lifetime of charge carriers, as further described in Section 2.6.

2.2. DFT calculations

To compute the electronic band structures and phonon dispersions of silicene and germanene, we rely on first principles density functional theory, using the plane-wave-
Figure 4. Effect of spin-orbit coupling on the electronic band structure of silicene (left) and germanene (right). Insets indicate main differences between calculated band structures with (black) and without (red) spin-orbit coupling (values are taken from Ref. (17))

based VASP code (35; 36). We use the local density approximation (LDA) to relax the structures and compute phonon frequencies, as it is well established that the LDA gives a quantitatively reliable description of these properties in solids. In contrast, we compute the electronic band structures using the HSE06 hybrid functional (37; 38), as hybrid functionals yield more accurate electronic band structures than the LDA (39–42). Note, that the optimized structural parameters, shown in Table 1 are in good agreement between LDA and HSE06, further reinforcing the expectation that LDA is accurate enough to describe the atomic structure in these materials. The structural optimization using the LDA and HSE06 functional is performed on a $30 \times 30 \times 1$ and $18 \times 18 \times 1$ Γ-centred Monkhorst-Pack grid (43), respectively, until all atomic forces decrease below 0.003 eV/Å. The plane-wave cutoff energy is set to 700 eV in all calculations.

In Fig. 4 we show the band structure of silicene and germanene with spin-orbit coupling (SOC) taken into account in order to investigate its effects and determine whether it needs to be included in the TB model and thus in the Raman calculations. In the case of silicene the band structure is rather unperturbed by the SOC (17; 18; 44; 45) apart from the relatively small 1.55 meV and 34 meV splitting introduced at the K and Γ points, respectively. These values are negligible next to the relevant Raman excitation energies (1 eV-3 eV), therefore we do not include SOC in our TB model for silicene. However, as the strength of SOC increases with the fourth power of the atomic number, in the case of germanene a much larger effect is expected. Several theoretical works (8; 17) indeed suggest that a 24 meV spin-orbit gap opens at the K point, however, compared to the relevant excitation energies (1 eV-3 eV) this is still negligible. On the other hand, SOC lifts the fourfold degeneracy of the highest valence bands at the Γ point, splitting them into two Kramers doublets separated by a significant energy of 196 meV. This latter effect can be explained by recognizing that in the first order SOC mixes spin states of different $p$ type orbitals, while transition between spin states on $p_z$
orbitals located on different atoms occurs in the second order through SOC coupling between \( p_z \) and \( p_x, p_y \) states followed by a hopping transition between the \( p_x, p_y \) states and the neighbouring \( p_z \) states. This effective coupling between \( p_z \) orbitals located on neighbouring atoms can lift the degeneracy at the K point. Its magnitude, however, is small compared to the mixing of \( p_x, p_y \) orbitals at the \( \Gamma \) point.

Vibrational properties are calculated using the LDA functional. The phonon dispersion relation is obtained by calculating the Hessian matrix of a \( 7 \times 7 \) supercell within the frozen phonon approximation using a \( 6 \times 6 \times 1 \) \( \Gamma \)-centred Monkhorst-Pack grid. The atomic displacements are set to 0.01 Å. Main features and phonon frequencies between the high symmetry points shown in Fig. 5 are in agreement with previous theoretical results (18; 46; 47).

2.3. Tight-binding model of silicene and germanene

To describe Raman scattering in silicene and germanene, we first construct a TB Hamiltonian with 4-orbital (\( s, p_x, p_y, p_z \)) basis on each atom, expressed as

\[
|\psi_{n,k}\rangle = \sum_{i,j} e^{ikR_i} c_{n,i,j}(k) | \varphi_j(r-R_i) \rangle,
\]

or in the second quantized formalism as

\[
|\psi_{n,k}\rangle = a_{n,k}^\dagger |0\rangle = \sum_{i,j} e^{ikR_i} c_{n,i,j}(k) a_{i,j}^\dagger |0\rangle,
\]

where \( R_i \) is the atomic position of the \( i \)th atom, |\( \varphi_j(r-R_i) \rangle \) is the \( j \)th basis centred on the \( i \)th atom, \( a_{i,j}^\dagger \) is the creation operator of an electron on the \( j \)th basis centred on the \( i \)th atom, \( a_{n,k}^\dagger \) is the creation operator on the \( n \)th band with lattice momentum of \( k \), and \( c_{n,i,j}(k) \) are the \( i,j \)th component of \( n \)th solution (\( c_n(k) \)) of the non-orthogonal Schrödinger equation:

\[
\hat{H}(k)c_n(k) = \epsilon_n(k)\hat{S}(k)c_n(k),
\]
Figure 6. Comparison of the characters of the DFT band structure and the fitted TB model for silicene (a,c) and germanene (b,d)

where $\hat{H}(k)$ and $\hat{S}(k)$ are the tight-binding Hamiltonian and overlap matrices, respectively, and $\epsilon_n(k)$ is the $n$th eigenvalue. Overlap matrix elements between orbitals centred on different atoms are integrated numerically using hydrogen-like orbitals with effective nuclear charges \( \text{[48]} \). The Hamiltonian is built by using the Slater-Koster method \( \text{[49]} \), taking up to third-nearest neighbour hopping interaction into account. Three on-site parameters are used to describe the different atomic energies of the orbitals, as the $p_x$ and $p_y$ on-site matrix elements are connected by symmetry.

Within the Slater-Koster method \( \text{[49]} \) the Hamiltonian and the overlap matrix elements can be written as

$$
\hat{H}_{i,i'}(k) = \sum_{l} \sum_{\text{3rd NN}} \int d^3 r \phi_{i'}^* (r - r_L) \hat{H} \phi_i (r - r_l) e^{ik(r_l - r_L)} a_{i,L}^\dagger a_{i,L} + \sum_{l} \int d^3 r \phi_{i'}^* (r - r_l) \hat{H} \phi_i (r - r_l) a_{i',L}^\dagger a_{i,L},
$$

(8)
where summation over \( l \) goes over a unit cell, summation over \( L \) goes over surrounding atoms in the crystal up to the third nearest neighbours, \( \varepsilon_{t'i} \) are the on-site terms of each atomic orbital, while \( t_{t'i}(r_l - r_L) \) and \( s_{t'i}(r_l - r_L) \) are the hopping and overlap integrals, respectively, between atoms located at \( r_l \) and \( r_L \).

The hopping parameters are fitted to the DFT results within a \( \pm 2 \) eV range around the Fermi level. The rest of the band structure is ignored during the fitting process as we are interested in reproducing the optical transitions within the relevant regime (1 eV – 3 eV). This assumption can be justified by the fact that the transitions between low and high energy bands would be suppressed by the energy denominators in Eqns 1 and 2. During the fitting procedure we acquire several parameter sets using the least squares approach, which reproduces the first principles band structures fairly well. In the final step, we compare the wavefunction characters of the DFT data and the TB model and we chose the parameter set which best reproduces the characters of the DFT calculation. This is extremely important for the calculation of the Raman intensities as the magnitude of the matrix elements, and therefore the transition probabilities, are mainly determined by the characters of the wavefunctions.

As stated in Section 2.2, in the tight binding model of germanene we take SOC into account between \( p \) orbitals. We implement this using the atomic matrix elements of the \( \hat{L}\hat{S} \) operator on the \( |p_x \uparrow \rangle, |p_x \downarrow \rangle, |p_y \uparrow \rangle, |p_y \downarrow \rangle, |p_z \uparrow \rangle, |p_z \downarrow \rangle \) basis,

\[
\hat{H}_{SOC} = \frac{\lambda_{SOC}}{2} \begin{pmatrix}
0 & 0 & -i & 0 & 0 & 1 \\
0 & 0 & 0 & i & -1 & 0 \\
i & 0 & 0 & 0 & 0 & -i \\
0 & -i & 0 & 0 & -i & 0 \\
0 & -1 & 0 & i & 0 & 0 \\
1 & 0 & i & 0 & 0 & 0
\end{pmatrix}
\]

(10)

The SOC parameter \( \lambda_{SOC} \) is chosen to reproduce the numerical value of the HSE06 gap at the \( \Gamma \) point, that is, \( \lambda_{SOC} = 196 \text{meV} \).

The fitted hopping integrals and calculated overlaps for silicene and germanane are shown in Tables 2 and 3, respectively. The characters presented in Fig. 6 show that the Dirac-like band of both silicene and germanene mostly contains \( s \) and \( p_z \) character, whilst the \( p_x, p_y \) character is suppressed. The mixing of \( s \) and \( p_z \) dominated bands is expected from the DFT calculations as the buckled structure yields the mixing of \( sp^2 \) hybrid orbitals with the \( p_z \) orbital. Moreover, in the case of silicene the flat conduction band around the M point also possesses \( s \) and \( p_z \) character, and optical transitions between the Dirac-like valence band and this band are allowed. The excitation energy of \( E_{pl}^{Si} = 2.12 \) eV between the Dirac-like bands at the M point is usually referred to as the \( \pi \) plasmon energy; we will refer to the \( E_{pl,2}^{Si} = 2.77 \) eV excitation energy between the valence band and the higher conduction band as the second \( \pi \) plasmon energy. In
Resonance Raman spectroscopy of silicene and germanene

|                | $s$  | $p_x$ | $p_y$ | $p_z$ |
|----------------|------|-------|-------|-------|
| On-site        | -2.451 | -0.198 | -0.198 | -0.055 |
| Hopping        | $t_{ss\sigma}$ | $t_{sp\sigma}$ | $t_{pp\sigma}$ | $t_{ss\pi}$ |
| 1st neighbour  | -1.675 | 2.868 | 3.207 | -1.372 |
| 2nd neighbour  | -0.793 | 0.605 | 0.721 | -0.019 |
| 3rd neighbour  | -1.165 | 0.859 | 0.982 | -0.104 |
| Overlap        | $s_{ss\sigma}$ | $s_{sp\sigma}$ | $s_{pp\sigma}$ | $s_{ss\pi}$ |
| 1st neighbour  | 0.031 | 0.032 | -0.036 | 0.022 |
| 2nd neighbour  | 0.003 | 0.005 | -0.003 | 0.001 |
| 3rd neighbour  | 0.002 | 0.004 | -0.002 | 0.001 |

Table 2. Fitted tight-binding (eV) and calculated overlap parameters of silicene

|                | $s$  | $p_x$ | $p_y$ | $p_z$ |
|----------------|------|-------|-------|-------|
| On-site        | -8.189 | 0.327 | 0.327 | 0.619 |
| Hopping        | $t_{ss\sigma}$ | $t_{sp\sigma}$ | $t_{pp\sigma}$ | $t_{ss\pi}$ |
| 1st neighbour  | -2.040 | 3.080 | 2.933 | -1.089 |
| 2nd neighbour  | 0.317 | 0.254 | 0.604 | -0.180 |
| 3rd neighbour  | 0.117 | 0.339 | 0.218 | -0.137 |
| Overlap        | $s_{ss\sigma}$ | $s_{sp\sigma}$ | $s_{pp\sigma}$ | $s_{ss\pi}$ |
| 1st neighbour  | 0.043 | 0.047 | -0.047 | 0.029 |
| 2nd neighbour  | 0.009 | 0.008 | -0.005 | 0.002 |
| 3rd neighbour  | 0.006 | 0.007 | 0.002 | 0.002 |

Table 3. Fitted tight-binding (eV) and calculated overlap parameters of germanene

In the case of germanene we find that although the $\pi$ plasmon energy of $E_{pl}^{Ge} = 2.12$ eV is lower compared to that of silicene, the second plasmon energy of $E_{pl,2}^{Ge} = 3.31$ eV is significantly higher. As this energy is larger than the relevant energy range, we neglect this band during the fitting procedure. On the other hand, at the $\Gamma$ point of germanene in-plane polarised optical transitions of 1.61 eV and 1.82 eV can be found between the mostly $s$ and $p_z$ conduction band and the SOC-perturbed $p_x$ and $p_y$ valence bands. Therefore, two resonances can be expected in the Raman spectra of germanene, and the splitting between them gives the on-site spin-orbit coupling strength. This effect is suppressed in silicene as the SOC strength is around one order of magnitude smaller compared to germanene, and the corresponding excitation energy of 4.45 eV is too large for the regime accessible in typical Raman measurements.
2.4. Matrix elements

The electron-photon matrix elements are numerically evaluated on the atomic basis set using the interaction Hamiltonian

$$\hat{H}_{e-p} = \frac{e\hbar}{im} \sum_{n,m,k,q} \frac{\partial}{\partial r_\lambda} \sqrt{\frac{\hbar}{2\omega_\epsilon_0}} e^{-iqr} \left\{ e_\lambda b_\lambda(-q) + e_\lambda^* b_{\lambda}^\dagger(q) \right\} a_{n,k-q}^\dagger a_{m,k}, \quad (11)$$

where $e_\lambda$ is the $\lambda$th component of polarization vector $e$, $b_{\lambda}^\dagger(q)$ and $b_\lambda(q)$ are the bosonic creation and annihilation operators of a photon with momentum $q$ and frequency $\omega$ in the dielectric environment described by $\epsilon_0$ dielectric constant and $A(q,r)$ is the vector potential of the photon. Since the vector potential in the long wavelength limit ($q \approx 0$) is independent of the coordinates ($A(q,r) \approx A(0,0)$), we compute the electron-photon matrix element by calculating the transition matrix elements of the $\nabla$ operator between the atomic orbitals. In usual experimental setups only backscattering photons are measured, therefore we calculate the in-plane components of the matrix element between the atomic orbitals. The integrals are evaluated between atomic sites up to third-nearest neighbours in accordance with our tight-binding model. Similarly to previous theoretical works [50, 51] we find that the largest matrix elements are between nearest-neighbours; this is due to the overlap between the orbitals decaying exponentially with increasing distance, and numerous on-site transition matrix elements being forbidden by symmetry.

The electron-photon matrix element can be expressed as

$$M_{Al}^{e-p} = \langle \psi_{n,k} | \hat{H}_{e-p} | \psi_{m,k} \rangle = \frac{e\hbar}{im} \sum_{i,j,i',j',\lambda} e_{n,i,j'}^* c_{m,i,j}(k) c_{m,i,j}(k) \left\{ \frac{\partial}{\partial r_\lambda} \varphi_j(r-R_\lambda) \right\} \times \langle \psi_{n,k} | \hat{H}_{e-p} | \psi_{m,k} \rangle \quad (12)$$

which shows that in the approximation of a constant vector potential, the matrix element only allows electron-hole excitations where the two quasiparticles have the same $k$. Furthermore, the conservation rule of lattice momentum $k$ during electron-photon interaction means that in order to absorb or emit a photon, the first $A$ and last $C$ virtual state involved in Eqs (11) and (12) should include an electron and a hole with the same $k$.

Next we calculate the electron-phonon matrix element $M_{CB}^{e-ph,\mu}$ describing the emission of a phonon from band $\mu$ with momentum $q$, which we obtain numerically from the interaction Hamiltonian,

$$\hat{H}_{e-ph,\mu} = \sum_{l,n,m,k,q} \sqrt{\frac{\hbar}{2M_l\omega_\mu}} \frac{\partial V_{e-ion}(r-R_\lambda)}{\partial R_l} Q_{\mu,l}(q) e^{-iqr} \times$$

$$\times \left\{ d_{\mu}^\dagger(-q) + d_{\mu}^\dagger(q) \right\} a_{n,k-q}^\dagger a_{m,k}, \quad (13)$$

where $d_{\mu}^\dagger(-q)$ and $d_{\mu}^\dagger(q)$ are the creation and annihilation operators of a phonon with momentum $q$ on the $\mu$ phonon band, $V_{e-ion}$ is the electron-ion potential, $M_l$ is the mass
of the nuclei positioned at $\mathbf{R}_l$, $\omega_{\mu}$ is the frequency of the phonon with $\mathbf{Q}_{\mu,l}(\mathbf{q})$ normal mode. The matrix elements of the derivative of the electron-ion potential on our basis are calculated by (51). In our tight-binding formalism the matrix element between different electronic bands can be written as

$$M_{CB}^{e-ph,\mu} = \langle \psi_{n,k-q} | \hat{H}_{e-ph,\mu} | \psi_{m,k} \rangle =$$

$$\sum_{i,i',j,j',l} \sqrt{\frac{\hbar}{2M_i \omega_{\mu}}} e_{n,i',j'}^*(\mathbf{k} - \mathbf{q}) c_{m,j,i}(\mathbf{k}) Q_{\mu,l}(\mathbf{q}) \times$$

$$\langle \varphi_{j'}(\mathbf{r} - \mathbf{R}_{l'}) \left| \frac{\partial V_{e-ion}(\mathbf{r} - \mathbf{R}_l)}{\partial \mathbf{R}_l} \right| \varphi_{j}(\mathbf{r} - \mathbf{R}_l) \rangle e^{i k \mathbf{R}_l} e^{-i(k-q) \mathbf{R}_{l'}} e^{-iq \mathbf{R}_l} \times$$

$$\times \{ d_{\mu}(\mathbf{q}) + d_{\mu}^{\dagger}(-\mathbf{q}) \} a_{i',j'}^{\dagger} a_{i,j}. \tag{14}$$

Using these matrix elements the two phonon (pp) spectra can be straightforwardly calculated, however to describe the defect induced (pd) Raman spectra a model of defect scattering is also needed. To this end, we introduce defect scattering operators, the matrix elements of which can model the effects of different types of point defects.

### 2.5. Defect scattering

We model defect induced Raman scattering through a variety of possible point defects that may occur in silicene or germanene. From an experimental point of view, four categories of point defects can be distinguished: substitutional atoms, Stone-Wales defects, adatoms, and vacancies. Within the framework of our tight-binding model, there are two ways in which we can describe scattering through such defects: the perturbative approach, and the scattering potential approach.

In the perturbative approach we introduce small perturbations into the tight-binding parameters. In this method, two types of scattering matrix elements can be defined: on-site and hopping scatterers. In either case, the corresponding tight-binding parameter is changed, resulting in a small perturbation of the system. The on-site scattering Hamiltonians perturb the on-site energy of a given orbital, while the hopping scattering Hamiltonians change a Slater-Koster hopping parameter. In our model we use 3 on-site parameters on every atom and 4 non-equivalent hoppings between atoms. Since the main contribution to the electron-photon and electron-phonon matrix elements arises from nearest-neighbour interaction, we only take into account defect scattering induced by changes in the on-site terms or in the nearest-neighbour hopping integrals. The defect scattering Hamiltonians for a nearest-neighbour hopping perturbation and for an on-site perturbation located on $\mathbf{R}_0$, respectively, can be written as

$$M_{BA}^t = \langle \psi_{n,k-q} | \hat{H}_t | \psi_{m,k} \rangle = \sum_{j,j',l} \sum_{j'\prime}^\text{1st NN} c_{n,j',j'}^*(\mathbf{k} - \mathbf{q}) c_{m,0,j}(\mathbf{k}) \times$$

$$\times \delta_{jj'}(\mathbf{R}_l') e^{i k \mathbf{R}_0} e^{-i(k-q) \mathbf{R}_{l'}} a_{j'}^{\dagger} a_{0,j}. \tag{15}$$

$$M_{BA}^e = \langle \psi_{n,k} | \hat{H}_e | \psi_{m,k} \rangle = \sum_j c_{n,0,j}(\mathbf{k}) c_{m,0,j}(\mathbf{k}) \delta \varepsilon_j a_{0,j}^{\dagger} a_{0,j}. \tag{16}$$
Resonance Raman spectroscopy of silicene and germanene

The above method can be used to describe a variety of real defects in the crystal. Substitutional impurities mostly change the atomic ionisation energies, Stone-Wales defects perturb the in-plane $\sigma$ bonds (52, 53), adatoms mostly change $\pi$ orbitals (53), whilst vacancies remove a site which eliminates an on-site term from the Hamiltonian along with the corresponding nearest-neighbour hopping terms (53). Therefore, the $t_{ss\sigma}$ and $t_{p\sigma\sigma}$ defects combined can be used to describe the presence of adatoms, $t_{s\sigma}$ and $t_{pp\pi}$ defects together can provide a quantitative model of Stone-Wales defects, and a change in the on-site matrix elements can model substitutional impurities. Vacancies could in principle be described through a combination of on-site and hopping scattering, but since this defect produces strong, local effects, it is not suitable to describe them through the perturbative approach.

Therefore, for vacancies, we use the scattering potential approach instead. In this method, rather than perturbing the parameters in the model, we introduce a scattering electron-ion potential that can be used to model the presence of a vacancy in the crystal. The scattering potential has the same form as the atomic potential used in the electron-phonon coupling in Eq. 14, which allows us to express scattering by a vacancy located at the position $R_v$ as

$$M_{BA}^{\text{vac}} = \langle \psi_{n,k-q} | \hat{H}_{\text{vac}} | \psi_{m,k} \rangle = \sum_{i,i',j,j'} c_{n,i',j'}^* (k-q) c_{m,i,j} (k) \times$$

$$\times \langle \varphi_{j'} (r - R_{j'}) | V_{\text{e-ion}} (r - R_v) | \varphi_{j} (r - R_i) \rangle e^{ikR_v} e^{-i(k-q)R_{j'} a_{j'}^\dagger a_{i,j}}. \tag{17}$$

Note, that the scattering potential approach is also useful for the description of substitutional defects, if said defects introduce strong, local changes to bonding in the crystal which cannot be accurately described by the perturbative approach.

2.6. Lifetime of charge carriers

The imaginary part of the energy denominators are calculated by taking into account the scattering of charge carriers using Fermi’s golden rule. In leading order (29) the
electron-phonon interaction determines the lifetime of excitations, while contributions from electron-photon interaction and even defect scattering can be neglected, the former due to the negligible momentum transfer during optical transitions, and the latter under the assumption of low defect concentration. In this approximation the inverse electronic lifetime can be calculated as

$$\gamma_{mk} = \frac{2\pi}{N_q} \sum_{\nu,q,m} \left| \langle \psi_{n,k-q} | \hat{H}_{e-ph,\nu} | \psi_{m,k} \rangle \right|^2 \delta(\epsilon_{mk} - \epsilon_{nk-q} - \hbar\omega_\nu(q)),$$  \hspace{1cm} (18)

where $N_q$ is the number of $q$ points used in the Brillouin zone integration. In order to simplify the calculations we remove the $k$-dependence from $\gamma$ by taking an average over the electron-hole pairs which can be excited at a given laser energy (29; 33) as

$$\gamma(\epsilon_L) = \frac{1}{N_k} \sum_{n,m,k} (\gamma_{nk} + \gamma_{mk}) \delta(\epsilon_L - (\epsilon_{nk} - \epsilon_{mk})),  \hspace{1cm} (19)$$

where $N_k$ is the number of $k$ points taken into account in the summation, $\epsilon_L$ is the exciting laser energy, and the Dirac $\delta(x)$ is approximated with a Gaussian function with 0.05 eV standard deviation. To calculate $\gamma(\epsilon_L)$ we use a 360 $\times$ 360 $\times$ 1 $\Gamma$-centred Monkhorst-Pack grid in the Brillouin zone for the electronic $k$ points and a 180 $\times$ 180 $\times$ 1 $\Gamma$-centred Monkhorst-Pack set for the phonon $k$ points.

The energy dependence of $\gamma(\epsilon_L)$ for silicene and germanene is shown in Fig. 7. The inverse lifetime of silicene shows similar dependence in the low energy ($< 2$ eV) region as previous works suggest (33). A resonance can be found at the $\pi$ plasmon energy (depicted by the dashed line) as expected from the band structure. A second resonance is visible at the second $\pi$ plasmon energy, as expected due to the large density of states arising from the flat conduction band near the $M$ point.

In the case of germanene, as illustrated in Fig. 7, only one resonance can be found near the excitation energy of the $\pi$-plasmon. The absence of the resonance of the second $\pi$ plasmon is due to the fact that its excitation energy is approximately 1 eV higher than that of silicene, thus it drops out of the relevant range. However as the $\Gamma$ point gap is smaller compared to silicene, a twin-resonance is expected due to the SOC. The apparent absence of this feature can be explained by taking into account two factors: the relatively lower electron-phonon coupling strength between states of $p_x, p_y$ character compared to the dominantly $s, p_z$ bands, and the small difference between the excitation energies at the $\Gamma$ point (1.61 eV, 1.82 eV) and at the $M$ point (2.12 eV). The former results in smaller transition matrix elements, thereby a reduced contribution to the lifetime, whilst the latter indicates that the overlap between resonances makes it difficult to separate them. The latter argument is supported by the highly asymmetric shape of the resonance compared to the inverse lifetime of silicene.

3. Two-phonon Raman spectra

Apart from the plasmon excitations, resonance condition occurs only in a small area of the Brillouin zone, therefore, a dense $k$ point grid is needed to calculate the Raman
Figure 8. Two-phonon Raman spectra of silicene (a) and germanene (b): Characteristic spectra at a few widely used excitation laser energies (left) and the full resonance profile (right).

spectra. In our model we achieve convergence with integration over a $360 \times 360 \times 1$ Monkhorst-Pack grid in the electronic $k$ space (virtual states) and a $180 \times 180 \times 1$ Monkhorst-Pack grid in the phonon $k$ space (final states).

Recently, a comparative study of two phonon Raman processes in graphene and silicene was published (33), based on a non-orthogonal tight-binding model (30) to calculate the electronic and vibrational properties. This approach utilized tight-binding parameters based on previous studies on silicon (54) and carbon (55) dimers which can describe the low energy electronic properties accurately, but the model neglects contributions from the second lowest conduction band at the M point, and there are missing features in the energy range of visible light (1.8 eV-3 eV). In comparison, using our model, which is parametrized from first principles density functional theory and takes the second conduction band at the M point into account, we obtain similar but different results.

In Fig. 8a we present the normalized two-phonon Raman spectra of silicene
Resonance Raman spectroscopy of silicene and germanene

at commonly used laser excitation energies. For better visibility of the low energy (< 1000 cm\(^{-1}\)) peaks, their region is enhanced by a factor of 10. At lower excitation energies (1eV-2eV), electron-hole excitations can occur on the Dirac cone near the K points, resulting in phonons that originate from the vicinity of the K point when charge carriers are scattered between neighbouring Dirac cones (inter-valley processes) and from the Γ point when scattering occurs within the same Dirac cone (intra-valley processes). As shown in the right panel of Fig. 8a, in this region the spectrum is dominated by two peaks around 1100 cm\(^{-1}\): the 2TO peak with phonons originating from the K point (\(\approx 1080\) cm\(^{-1}\)) and the 2LO peak with phonons originating from the Γ point (\(\approx 1120\) cm\(^{-1}\)). By increasing the excitation energy, location of electron-hole pairs on \(k\)-space shifts towards the M point, which pushes the phonon wave vector towards the M point as well, and consequently merges the 2TO and 2LO peaks as can be seen on the lowest energy spectrum in Fig. 8a. At the first plasmon energy electron-hole pairs can be excited from a wide area of the Brillouin zone, resulting in activation of multiple peaks from various regions.

These results are consistent with the findings of Ref. (33), however, at larger excitation energies our spectra differ from those in Ref. (33). The difference is due to the second plasmon, which only appears in our calculations as the model in Ref. (33) neglects the higher energy conduction band and does not take the M point into account. Similarly to the excitations involving the Dirac cones at low excitation energies, the second plasmon introduces charge carrier scattering between states belonging to the same M point (intra-valley) and between different M points (inter-valley). Intra-valley scattering at the M point yields phonons originating from the Γ point, while inter-valley M-point scattering results in phonons originating from the vicinity of the K point, which can be seen in the spectrum with the largest excitation energy in Fig. 8a.

The intensity and dispersion of the two main peaks are shown in Fig. 9. Below the excitation energy of 2 eV both peaks exhibit a linear dispersion similar to that of graphene. Around the plasmon energy the peaks converge on one another, making them difficult to separate between 2 – 2.3 eV. Above this energy range but below the second plasmon energy both peaks exhibit an increase in Raman shift within the range of 2.4 – 2.6 eV. Both peaks become approximately non-dispersive past the second plasmon energy, as expected from Fig. 5.

Due to resonance effects numerous peaks are also activated in the low energy region. Peaks visible at the lowest excitation energy can be identified as 2ZO bands resulted from both inter- and intra-valley scattering. The position and origin of these peaks agrees with the findings in Ref. (33). However, our model predicts quite different relative intensities for these peaks. One reason for the difference is that the second plasmon, which is missing from the model in Ref. (33), enhances these peaks and also introduces new peaks assigned as combination peaks of the ZO and in-plane bands as depicted in the largest excitation energy spectrum in Fig. 8. The second reason why we obtain different results is that the sublattice buckling in the silicene crystal is approximately 50% larger in Ref. (33) compared to our DFT results. First principles methods have been proven to yield
Figure 9. Dispersion of the main in-plane peaks of silicene (left) and germanene (right), point size indicates the intensity of peaks.

accurate structural parameters for germanene, matching experiments (15), therefore we expect that the LDA structures used in the present work provide quantitatively accurate predictions for the Raman spectra of germanene as well as silicene, which is expected to be described to similar accuracy by the LDA. In the Raman spectra of graphene the ZO phonon bands are suppressed, which implies that reduced sublattice buckling can be responsible for the relatively smaller intensity of ZO combination peaks in our calculations. Moreover, the sublattice buckling value calculated for germanene is closer to the value used in the previous work (33), thus a closer agreement can be expected in the relative intensity ratios.

We calculate the Raman spectra of silicene and germanene for excitation energies between 1 eV and 3 eV with an energy resolution of 0.05 eV. This is plotted on the right hand side in Fig. 8a-b, where the colours indicate the Raman intensity on logarithmic scale. The dispersion of the peaks can be clearly seen for high and low intensity peaks as well. Resonance effects in the overall and peak intensities are captured around both plasmonic excitations, and their effect on the spectra can be distinguished. Resonance with the $\pi$ plasmon occurs when electron-hole excitations take place around the flat band at the M point. At this energy the results of intra- and inter-valley processes merge, resulting in larger linewidth and integrated intensity. At the second $\pi$ plasmon energy, other scattering processes between M points are activated, resulting in larger overall intensity. Moreover, as the flat conduction band responsible to the second plasmon is mostly of $s$ character, it enhances the contribution of the out-of-plane modes due to non-zero coupling between $s$ electrons and ZO modes.

During double resonant processes the peak positions usually shift at different laser energies due to the different origin of phonons dictated by the double resonant condition. In the case of graphene this shift is on the order of 100 cm$^{-1}$/eV for the relevant peaks (29), while in the calculated excitation profile in Fig. 8 much lower shift can be found. This is the result of the smaller dispersion of the TO phonon band shown in Fig. 5 and
the overall smaller vibrational frequencies compared to graphene. The positions of the lower intensity peaks such as the 2ZO or LOZO peak exhibit larger shift in accordance with their calculated phonon dispersions in Fig. 5.

We show the calculated two-phonon Raman spectra of germanene in Fig. 8b for the same excitation energies as shown for silicene. Similarly the low energy spectra are dominated by the 2TO peak, however, the largest contribution originates from the Γ point, as both intra-valley processes and scattering between valence states located near Γ gives contribution to scattering with near Γ point phonons. Therefore relative contribution of inter-valley scatterings to the spectra is smaller although their presence can be captured in multiple peaks depicted in Fig. 8b. Low intensity ZO peaks are also present, even at the lowest excitation energy in Fig. 8b peaks composed of inter- and intra-valley scattered ZO phonons are visible. Their relative intensity ratio compared to the intensity of 2TO phonon peaks, is much closer to the ratio calculated for silicene in Ref. (33). This also confirms that the difference in buckling is responsible for the quantitative differences between our and the previous model.

Above the plasmon energy, other combination peaks become visible in the 200 cm\(^{-1}\)-500 cm\(^{-1}\) region. These peaks originate with no exception from the vicinity of the K point, as above the plasmon energy electron-hole excitations can occur around the M point and scattering between neighbouring M points result in emission of near K point phonons. Moreover, intensity of the ZO peaks show dramatic increase compared to the resonant spectra of silicene or graphene. The general enhancement of the out-of-plane peaks with larger buckling can be understood by taking into account the hybridization of the \(\pi\) electrons. By increasing the buckling, the \(\pi\) orbitals which have purely \(p_z\) character will hybridize with the \(s\) orbitals. The quantitative difference between \(s\) and \(p_z\) orbitals is that interaction between \(p_z\) orbitals and out-of-plane phonons is prohibited, whilst \(s\) orbitals do not distinguish between in-plane and out-of-plane modes, therefore, by increasing the \(s\) character, the intensity of ZO peaks will increase.

The resonance profile of the two-phonon spectra of germanene shown in Fig. 8b show similar trends as seen in the case of silicene. Similarly to the results of the lifetime calculation, resonance effect can only be found around the plasmon excitation energy, whilst the splitting of the bandgap by the SOC at Γ cannot be captured.

Finally we plot the dispersion of the main two in-plane peaks in Fig. 9. The dispersion of the 2TO peak originating from K point contains several linear dispersion regions, however, within the excitation energy range of 2–2.7 eV, unlike the previously investigated cases, the peak position shifts downwards with increasing laser energy. Similarly the 2TO peak originating from Γ point exhibits linear dispersion, however the amplitude of this dispersion is much smaller compared to the previous cases. Unlike in the case of silicene the peak originating from the Γ point shows a resonance in the intensity, whilst the peak originating from the K point does not exhibit an increase in intensity.
4. Defect induced Raman spectra

The calculated defect induced Raman spectra for silicene are shown in Fig. 10. We find a peak from ZO phonons, however, its intensity is small compared to the LO and TO peaks. In particular, Raman scattering induced by $t_{ss\sigma}$ and $t_{pp\pi}$ defects contain a wide background, rather than a distinguishable peak. In contrast, defects which perturb the $\sigma$ bonds ($t_{sp\sigma}$ and $t_{pp\sigma}$) activate this peak as shown in the left side of Fig. 10a-c. Moreover the $t_{pp\sigma}$ defect activates the TO peak with phonons originating from the $\Gamma$ point, this peak is only visible at this defect, therefore its presence is a clear indication of perturbations in the $t_{pp\sigma}$ matrix element.

In order to calculate comparable intensity for a given defect concentration, the magnitudes of the hopping and on-site defects are chosen to be equal. As shown in the right hand side of Fig. 10, the largest contribution results from $t_{pp\pi}$ defect, in accordance with the $p_z$ dominated electronic bands around the Fermi level. These bands, however, have a significant amount of $s$ character due to hybridization of $s$ and $p$ orbitals caused by the sublattice buckling, thus $t_{ss\sigma}$ and $t_{sp\sigma}$ defects can introduce similar (lower) intensities as plotted in Fig. 10a-b. The lowest overall Raman intensity results from $t_{pp\sigma}$ defects, as these hopping matrix elements describe bands well below the Fermi level.

Raman spectra of on-site defects are calculated by perturbing all on-site matrix elements on a given atom equally. Results shown in Fig. 10e resemble the $t_{pp\pi}$ induced defects in many ways: the spectra contain the wide background arising from ZO phonon band, and the absolute intensity is also remarkably high. Due to the $p_z$ dominated electronic bands, the largest Raman intensity is achieved by perturbing these atomic states, therefore by changing the on-site energy of each state equally results in scattering dominated by the $p_z$ orbital.

Vacancy induced spectra combine the effects of multiple hopping defects and the on-site defect: they are still dominated by the TO peak, with a somewhat distinguishable ZO peak, and at larger laser energies the TO peak originating from the $\Gamma$ point is visible as a shoulder.

Resonance profiles of these defects can provide guidelines to distinguish between them. Defects perturbing bonds including $t_{sp\sigma}$, $t_{pp\sigma}$ and the vacancy show enhanced intensity above the second plasmon energy. On the contrary defects perturbing $p_z$ orbitals exhibit a resonance near this energy, but no enhancement effect can be seen.

Defect induced spectra of germanene with the aforementioned defect scattering matrix elements are presented in Fig. 11. In general, the defect induced spectra of germanene show more features compared to silicene, similarly to the two phonon spectra. Due to the multiple activated peaks in the spectra, distinguishing different scatterers is easier. Results of hopping scatterers presented in Fig. 11 show that $t_{ss\sigma}$ and $t_{sp\sigma}$ defects do not activate the ZO peak originating from the $\Gamma$ point, but several peaks can be seen originating from the M point. These peaks are only present above the plasmon excitation energy, as presented in the right hand side of Fig. 11a-b. Although at the same point significant enhancement of TO peak can be caught, the absolute intensity of
Figure 10. Defect induced Raman spectra of silicene at selected laser excitation energies (left side) and excitation profiles on a logarithmic scale (right side) for different hopping scattering matrix elements: a) $t_{as\sigma}$, b) $t_{sp\sigma}$, c) $t_{pp\pi}$, d) $t_{pp\pi}$, e) On-site, f) Vacancy.
Figure 11. Defect induced Raman spectra of germanene at selected laser excitation energies (left side) and excitation profiles on a logarithmic scale (right side) for different hopping scattering matrix elements: a) $t_{ss\sigma}$, b) $t_{sp\sigma}$, c) $t_{pp\sigma}$, d) $t_{pp\pi}$, e) On-site, f) Vacancy.
these defects does not reach the intensity of the other defects. In the case of $t_{pp\sigma}$ and $t_{pp\pi}$, enhancement of the ZO peak originating from the Γ point is shown in Fig. 11c-d. As the spectra on the left hand side are normalized to the largest peak intensity, apparently the TO peak loses its intensity in the case of the $t_{pp\sigma}$ defect. From the examination of the excitation profile on the right hand side, it is evident that even though the TO peak is enhanced, the enhancement factor is relatively small.

On-site defect induced spectra in Fig. 11e show similar features to $t_{pp\pi}$, however, the LO peak intensity is remarkably higher. Spectra of vacancy induced scattering shown in Fig. 11f resemble the $t_{pp\sigma}$ defect, although the ZO intensity is even larger.

The ZO/TO intensity ratio for all considered defects is presented in Fig. 4. Although the intensity of the ZO peak on silicene is small, differences between defect scatterers is visible in Fig. 4a. Generally the ZO peak intensity can be correlated to the effect on the σ bonds, as larger ZO intensity is achieved for $t_{sp\sigma}$, $t_{pp\sigma}$, and vacancies. Resonances near the plasmon excitation energies are also visible, implying greater enhancement of the ZO intensity compared to the intensity of the TO peak. Similar resonance effect can be seen in the case of germanene at the plasmon energy, although resonance at the Γ gap value is not present. Similarly to silicene, the largest relative intensity can be achieved with $t_{pp\sigma}$ defects and vacancies, which perturb mostly the in-plane bonds. Similarly large intensity ratio can be found at the $t_{pp\pi}$ hopping defect, however, the ZO peak intensity does not reach the intensity of the TO peak, whilst the former defects induce larger ZO peak intensity above the plasmon energy. Finally, $t_{ss\sigma}$, $t_{sp\sigma}$ and the on-site defect introduce a ZO peak around one order of magnitude smaller than the ZO peak.

5. Conclusions

We used a tight-binding model parametrised from first principles density functional theory to describe resonant Raman scattering in silicene and germanene. We found that
spin-orbit coupling has a significant effect on the resonance profile of germanene, whereas spin-orbit is negligible in silicene. We showed that a second plasmon transition at the M point between the top valence band and the second lowest conduction band introduces an additional resonance in silicene. By analysing the two phonon spectra we derived a relation between sublattice buckling and the relative intensity ratio of the intensity of out-of-plane modes. We calculated the Raman response of defect induced single phonon scattering for substitutional atoms (on-site), Stone-Wales defects ($t_{sp\sigma}, t_{pp\sigma}$), adatoms ($t_{ss\sigma}, t_{pp\pi}$) and vacancies. We demonstrated that the relative intensity ratio of out-of-plane and in-plane vibrations can be exploited to identify the presence of these defects from the Raman spectrum.

6. Acknowledgements

Support from the Hungarian National Research, Development and Innovation Office (NKFIH, Grant No. K-108676 and K-115608) is acknowledged. We acknowledge [NIIF] for awarding us access to resource based in Hungary at Debrecen. This research was supported by the National Research Development and Innovation Office of Hungary within the Quantum Technology National Excellence Program (Project No. 2017-1.2.1-NKP-2017-00001). This work was completed in the ELTE Excellence Program (783-3/2018/FEKUTSRAT) supported by the Hungarian Ministry of Human Capacities. G. K. acknowledges support from the New National Excellence Program (UNKP) of the Ministry of Human Capacities in Hungary. V. Z. acknowledges support from the Graphene Flagship Project, the N8 Polaris service, the ARCHER National UK Supercomputer (RAP Project e547), and the Computational Shared Facility at the University of Manchester. J. K. acknowledges the Bolyai program of the Hungarian Academy of Sciences.

References

[1] Kyozaburo Takeda and Kenji Shiraishi. Theoretical possibility of stage corrugation in Si and Ge analogs of graphite. Physical Review. B, Condensed Matter, 50(20):14916–14922, 1994.

[2] M. Houssa, G. Pourtois, V. V. Afanasev, and A. Stesmans. Electronic properties of two-dimensional hexagonal germanium. Applied Physics Letters, 96(8):082111, February 2010.

[3] Bernard Aufray, Abdelkader Kara, Sébastien Vizzini, Hamid Oughaddou, Christel Léandri, Benedicte Ealet, and Guy Le Lay. Graphene-like silicon nanoribbons on Ag(110): A possible formation of silicene. Applied Physics Letters, 96(18):183102, May 2010.

[4] Paola De Padova, Claudio Quaresima, Carlo Ottaviani, Polina M. Sheverdyeva, Paolo Moras, Carlo Carbone, Dinesh Topwal, Bruno Olivieri, Abdelkader Kara, Hamid Oughaddou, Bernard Aufray, and Guy Le Lay. Evidence of graphene-like
electronic signature in silicene nanoribbons. *Applied Physics Letters*, 96(26):261905, June 2010.

[5] Boubekeur Lalmi, Hamid Oughaddou, Hanna Enriquez, Abdelkader Kara, Sébastien Vizzini, Bénédicte Ealet, and Bernard Aufray. Epitaxial growth of a silicene sheet. *Applied Physics Letters*, 97(22):223109, 2010.

[6] Patrick Vogt, Paola De Padova, Claudio Quaresima, Jose Avila, Emmanouil Frantzkeskakis, Maria Carmen Asensio, Andrea Resta, Bénédicte Ealet, and Guy Le Lay. Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional Silicon. *Physical Review Letters*, 108(15):155501, April 2012.

[7] Mickael Derivaz, Didier Dentel, Régis Stephan, Marie-Christine Hanf, Ahmed Mehdouii, Philippe Sonnet, and Carmelo Pirri. Continuous Germanene Layer on Al(111). *Nano Letters*, 15(4):2510–2516, April 2015.

[8] A. Acun, L. Zhang, P. Bampoulis, M. Farmanbar, A. van Houselt, A. N. Rudenko, M. Lingenfelder, G. Brocks, B Poelsema, M. I. Katsnelson, and H. J. W. Zandvliet. Germanene: the germanium analogue of graphene. *Journal of Physics: Condensed Matter*, 27(44):443002, 2015.

[9] A. Curcella, R. Bernard, Y. Borensztein, M. Lazzeri, A. Resta, Y. Garreau, and G. Prévot. Multilayer silicene: clear evidence of Ag-terminated bulk silicon. *2D Materials*, 4(2):025067, 2017.

[10] Tobias G. Gill, Antoine Fleurence, Ben Warner, Henning Prüser, Rainer Friedlein, Jerzy T. Sadowski, Cyrus F. Hirjibehedin, and Yukiko Yamada-Takamura. Metallic atomically-thin layered silicon epitaxially grown on silicene/ZrB 2. *2D Materials*, 4(2):021015, 2017.

[11] Pedro Borlido, Claudia Rödl, Miguel A. L. Marques, and Silvana Botti. The ground state of two-dimensional silicon. *2D Materials*, 5(3):035010, 2018.

[12] Chao Lian and Sheng Meng. Dirac cone pairs in silicene induced by interface Si-Ag hybridization: A first-principles effective band study. *Physical Review B*, 95(24):245409, June 2017.

[13] Niels B. M. Schröter, Matthew D. Watson, Liam B. Duffy, Moritz Hoesch, Yulin Chen, Thorsten Hesjedal, and Timur K. Kim. Emergence of Dirac-like bands in the monolayer limit of epitaxial Ge films on Au(1 1 1). *2D Materials*, 4(3):031005, 2017.

[14] Li Tao, Eugenio Cinquanta, Daniele Chiappe, Carlo Grazianetti, Marco Fanciulli, Madan Dubey, Alessandro Molle, and Deji Akinwande. Silicene field-effect transistors operating at room temperature. *Nature Nanotechnology*, 10(3):227231, February 2015.

[15] B. N. Madhushankar, A. Kaverzin, T. Giousis, G. Potsi, D. Gournis, P. Rudolf, G. R. Blake, C. H. van der Wal, and B. J. van Wees. Electronic properties of germanane field-effect transistors. *2D Materials*, 4(2):021009, 2017.
REFERENCES

[16] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric Field Effect in Atomically Thin Carbon Films. Science, 306(5696):666–669, 2004.

[17] Cheng-Cheng Liu, Hua Jiang, and Yugui Yao. Low-energy effective Hamiltonian involving spin-orbit coupling in silicene and two-dimensional germanium and tin. Physical Review B, 84(19):195430, November 2011.

[18] N. D. Drummond, V. Zólyomi, and V. I. Fal’ko. Electrically tunable band gap in silicene. Physical Review B, 85(7):075423, 2012.

[19] Thaneshwor Kaloni, Muhammad Tahir, and U Schwingenschlögl. Quasi freestanding silicene in a superlattice with hexagonal boron nitride. Scientific Reports, 3:3192, 2013.

[20] Motohiko Ezawa. Monolayer Topological Insulators: Silicene, Germanene, and Stanene. Journal of the Physical Society of Japan, 84(12):121003, October 2015.

[21] Jincheng Zhuang, Nan Gao, Zhi Li, Xun Xu, Jiaou Wang, Jijun Zhao, Shi Xue Dou, and Yi Du. Cooperative ElectronPhonon Coupling and Buckled Structure in Germanene on Au(111). ACS Nano, 11(4):3553–3559, April 2017.

[22] Jia-An Yan, Shang-Peng Gao, Ryan Stein, and Gregory Coard. Tuning the electronic structure of silicene and germanene by biaxial strain and electric field. Physical Review B, 91(24):245403, June 2015.

[23] T. Mohiuddin, A. Lombardo, R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. Basko, C. Galiotis, N. Marzari, K. Novoselov, A. Geim, and A. Ferrari. Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Gr¨uneisen parameters, and sample orientation. Physical Review B, 79(20):205433–205433, May 2009.

[24] G. Kukucska and J. Koltai. Theoretical Investigation of Strain and Doping on the Raman Spectra of Monolayer MoS2. physica status solidi (b), 254(11), November 2017.

[25] Ji Eun Lee, Gwanghyun Ahn, Jihye Shim, Young Sik Lee, and Sunmin Ryu. Optical separation of mechanical strain from charge doping in graphene. Nature Communications, 3:1024, August 2012.

[26] M. M. Lucchese, F. Stavale, E. H. Martins Ferreira, C. Vilani, M. V. O. Moutinho, Rodrigo B. Capaz, C. A. Achete, and A. Jorio. Quantifying ion-induced defects and Raman relaxation length in graphene. Carbon, 48(5):1592–1597, April 2010.

[27] C. Casiraghi, A. Hartschuh, H. Qian, S. Piscanec, C. Georgi, A. Fasoli, K. S. Novoselov, D. M. Basko, and A. C. Ferrari. Raman spectroscopy of graphene edges. Nano Letters, 9(4):1433–1441, April 2009.

[28] M. S. Dresselhaus, A. Jorio, A. G. Souza Filho, and R. Saito. Defect characterization in graphene and carbon nanotubes using Raman spectroscopy. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 368(1932):5355–5377, December 2010.
REFERENCES

[29] Pedro Venezuela, Michele Lazzeri, and Francesco Mauri. Theory of double-resonant Raman spectra in graphene: Intensity and line shape of defect-induced and two-phonon bands. *Physical Review B*, 84(3):1–28, July 2011.

[30] Valentin N. Popov and Luc Henrard. Comparative study of the optical properties of single-walled carbon nanotubes within orthogonal and nonorthogonal tight-binding models. *Physical Review B*, 70(11):115407, September 2004.

[31] R M Martin and L M Falicov. Resonant Raman scattering. In *Light Scattering in Solids I*, volume 8 of *Topics in Applied Physics*, pages 79–145. Springer Berlin Heidelberg, 1975.

[32] V Zólyomi, J Koltai, and J Kürti. Resonance Raman spectroscopy of graphite and graphene. *physica status solidi (b)*, 248(11):2435–2444, 2011.

[33] Valentin N. Popov and Philippe Lambin. Comparative study of the two-phonon Raman bands of silicene and graphene. *2D Materials*, 3(2):025014, 2016.

[34] C. Thomsen and S. Reich. Double Resonant Raman Scattering in Graphite. *Physical Review Letters*, 85(24):5214–5217, December 2000.

[35] G. Kresse and J. Hafner. *Ab initio* molecular dynamics for liquid metals. *Physical Review B*, 47(1):558–561, 1993.

[36] G. Kresse and J. Furthmüller. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Physical Review B*, 54(16):11169–11186, October 1996.

[37] Jochen Heyd, Gustavo E. Scuseria, and Matthias Ernzerhof. Hybrid functionals based on a screened Coulomb potential. *The Journal of Chemical Physics*, 118(18):8207–8215, April 2003.

[38] Jochen Heyd, Gustavo E. Scuseria, and Matthias Ernzerhof. Erratum: Hybrid functionals based on a screened Coulomb potential [J. Chem. Phys. 118, 8207 (2003)]. *The Journal of Chemical Physics*, 124(21):219906, June 2006.

[39] J. Muscat, A. Wander, and N. M. Harrison. On the prediction of band gaps from hybrid functional theory. *Chemical Physics Letters*, 342(3):397–401, July 2001.

[40] Jochen Heyd, Juan E. Peralta, Gustavo E. Scuseria, and Richard L. Martin. Energy band gaps and lattice parameters evaluated with the Heyd-Scuseria-Ernzerhof screened hybrid functional. *The Journal of Chemical Physics*, 123(17):174101, October 2005.

[41] Peter Dek, Blint Aradi, Thomas Frauenheim, Erik Janzén, and Adam Gali. Accurate defect levels obtained from the HSE06 range-separated hybrid functional. *Physical Review B*, 81(15):153203, April 2010.

[42] M. J. Lucero, T. M. Henderson, and G. E. Scuseria. Improved semiconductor lattice parameters and band gaps from a middle-range screened hybrid exchange functional. *Journal of Physics: Condensed Matter*, 24(14):145504, 2012.

[43] Hendrik J. Monkhorst and James D. Pack. Special points for Brillouin-zone integrations. *Physical Review B*, 13(12):5188–5192, June 1976.
[44] Cheng-Cheng Liu, Wanxiang Feng, and Yugui Yao. Quantum Spin Hall Effect in Silicene and Two-Dimensional Germanium. *Physical Review Letters*, 107(7):076802, August 2011.

[45] Ranber Singh. Spinorbit splitting in graphene, silicene and germanene: Dependence on buckling. *International Journal of Modern Physics B*, 32(05):1850055, November 2017.

[46] Chuanghua Yang, Zhongyuan Yu, Pengfei Lu, Yumin Liu, Han Ye, and Tao Gao. Phonon instability and ideal strength of silicene under tension. *Computational Materials Science*, 95:420–428, December 2014.

[47] Xu-Jin Ge, Kai-Lun Yao, and Jing-Tao Lü. Comparative study of phonon spectrum and thermal expansion of graphene, silicene, germanene, and blue phosphorene. *Physical Review B*, 94(16):165433, October 2016.

[48] E. Clementi and D. L. Raimondi. Atomic Screening Constants from SCF Functions. *The Journal of Chemical Physics*, 38(11):2686–2689, June 1963.

[49] J. C. Slater and G. F. Koster. Simplified LCAO Method for the Periodic Potential Problem. *Physical Review*, 94(6):1498–1524, June 1954.

[50] A. Grüneis, R. Saito, Ge. G. Samsonidze, T. Kimura, M. A. Pimenta, A. Jorio, A. G. Souza Filho, G. Dresselhaus, and M. S. Dresselhaus. Inhomogeneous optical absorption around the K point in graphite and carbon nanotubes. *Physical Review B*, 67(16):165402, April 2003.

[51] J. Jiang, R. Saito, Ge. G. Samsonidze, S. G. Chou, A. Jorio, G. Dresselhaus, and M. S. Dresselhaus. Electron-phonon matrix elements in single-wall carbon nanotubes. *Physical Review B*, 72(23):235408, December 2005.

[52] H. Sahin, J. Sivek, S. Li, B. Partoens, and F. M. Peeters. Stone-Wales defects in silicene: Formation, stability, and reactivity of defect sites. *Physical Review B*, 88(4):045434, July 2013.

[53] Wei Zhang, Wen-Cai Lu, Hong-Xing Zhang, K. M. Ho, and C. Z. Wang. Tight-binding calculation studies of vacancy and adatom defects in graphene. *Journal of Physics: Condensed Matter*, 28(11):115001, 2016.

[54] Th. Frauenheim, F. Weich, Th. Köhler, S. Uhlmann, D. Porezag, and G. Seifert. Density-functional-based construction of transferable nonorthogonal tight-binding potentials for Si and SiH. *Physical Review B*, 52(15):11492–11501, October 1995.

[55] D. Porezag, Th. Frauenheim, Th. Köhler, G. Seifert, and R. Kaschner. Construction of tight-binding-like potentials on the basis of density-functional theory: Application to carbon. *Physical Review B*, 51(19):12947–12957, May 1995.