Effect of Surface States and Breakdown of the Schottky-Mott Limit of Graphene/Silicon van der Waals Heterostructure

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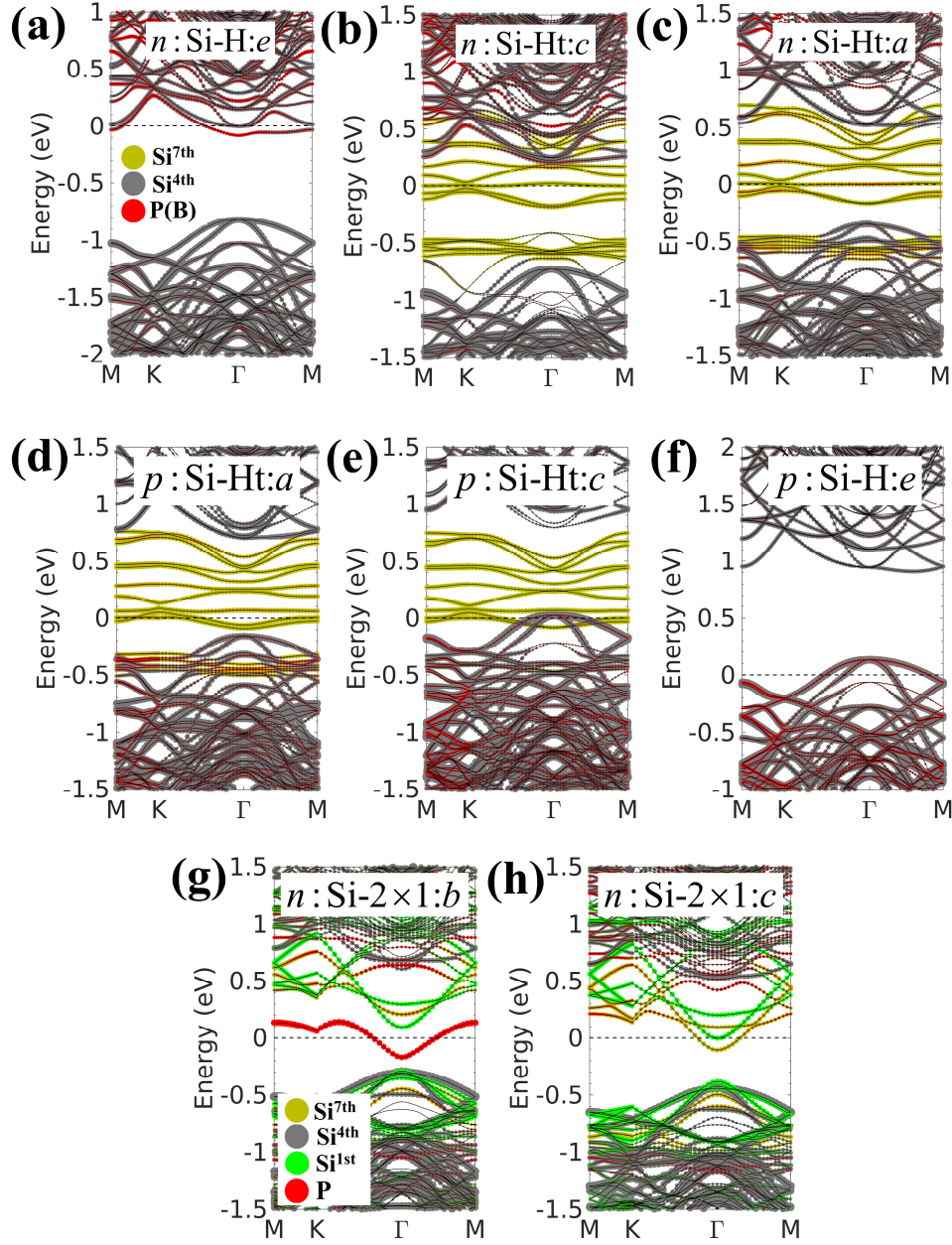
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Figure S1. Projected band structures of the Si substrates for (a) *p*:Si-H:*e,* (b) *p*:Si-Ht:*c*, (c) *p*:Si-Ht:*a*, (d) *n*:Si-Ht:*a*, (e) *n*:Si-Ht:*c* and (f) *n*:Si-H:*e*; for (g) *n*:Si-2×1:*b*, and (h) *n*:Si-2×1:*c*. The yellow, gray, green, and red dots represent the projection of Si^{7th}, Si^{4th}, Si^{1st} layers and P(B) dopant atom, respectively. The projection weight is represented by the dot size. The projection weight of P(B) dopant atom is multiplied by a factor of 5 for better visualization. For the Si-2×1 substrates (figure (g) and (h)), the Si^{1st} layer consists of the π_t and π_t* bands; and the Si^{7th} layer consists of the π_b and π_b* bands. The Fermi level is set at $E = 0$ eV.
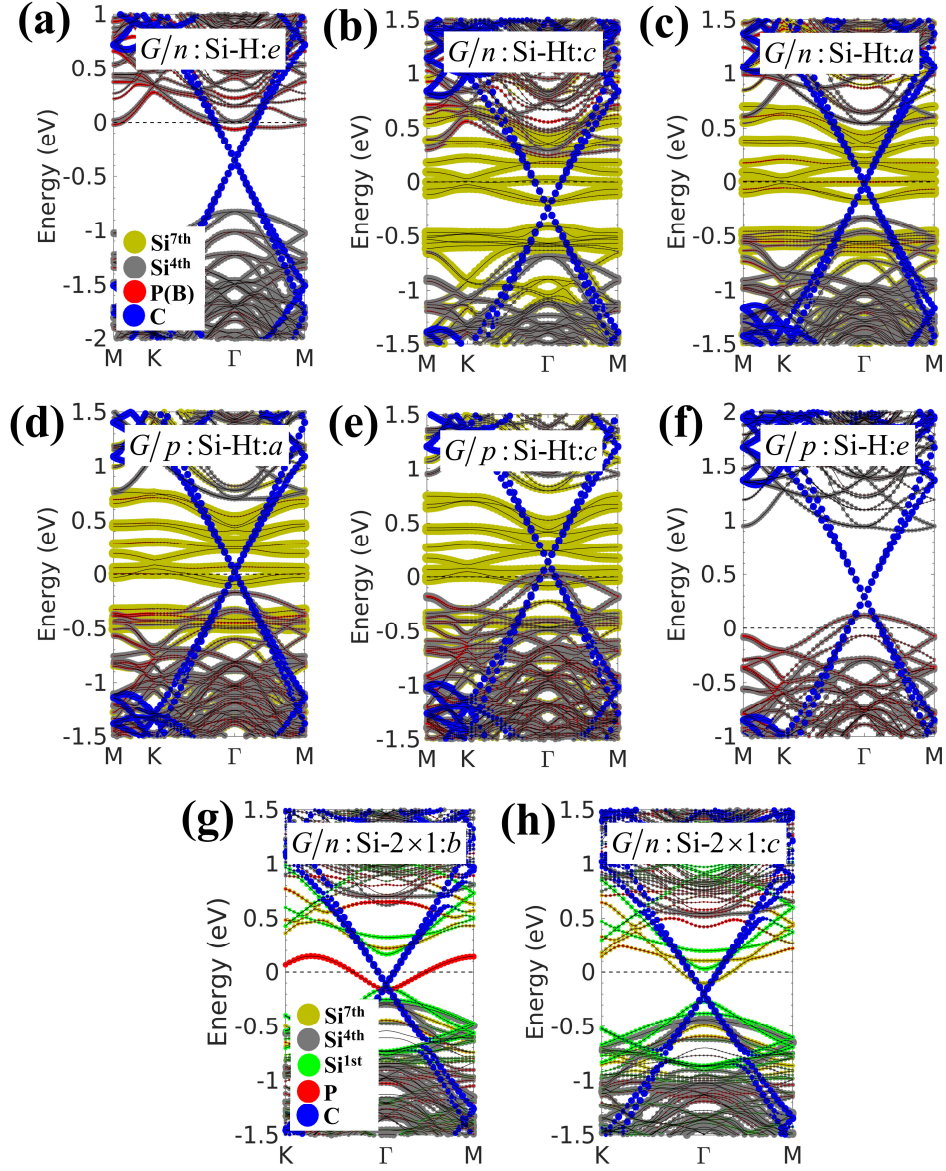
Figure S2. Projected band structures of the G/Si interfaces for (a) G/*p*:Si-H:*e*, (b) G/*p*:Si-Ht:*c*, (c) G/*p*:Si-Ht:*a*, (d) G/*n*:Si-Ht:*a*, (e) G/*n*:Si-Ht:*c* and (f) G/*n*:Si-H:*e*; for (g) G/*n*:Si-2×1:*b*, and (h) G/*n*:Si-2×1:*c*. The yellow, gray, green, red, and blue dots represent the projection of Si^{7th}, Si^{4th}, Si^{1st} layers, P(B) dopant atom, and C atoms, respectively. The projection weight is represented by the dot size. The projection weight of P(B) dopant atom is multiplied by a factor of 5 for better visualization. For the G/Si-2×1 interfaces (figure (g) and (h)), the Si^{1st} layer consists of the π_t and π_t* bands; and the Si^{7th} layer consists of the π_b and π_b* bands. The Fermi level is set at $E = 0$ eV.
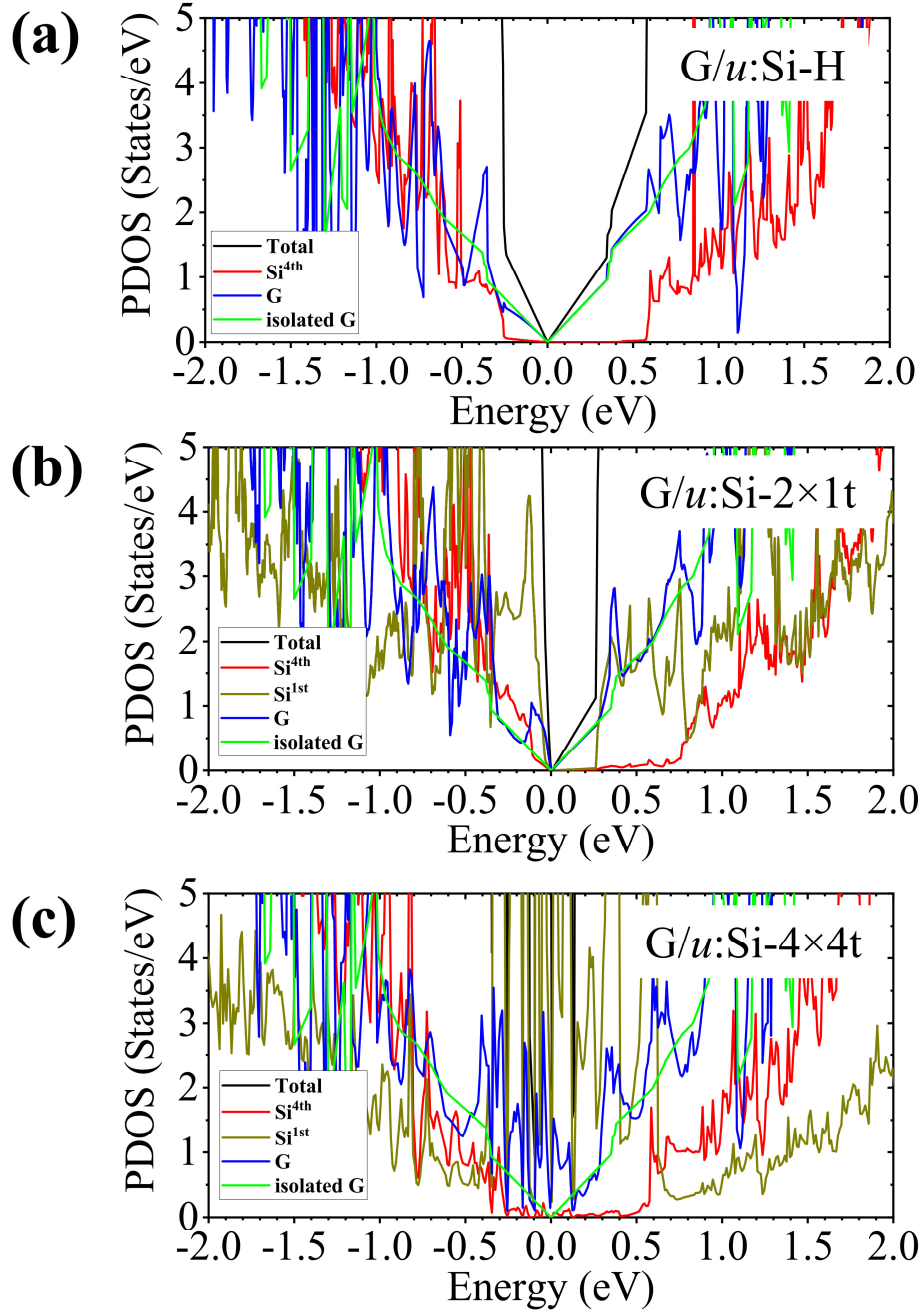
Figure S3. Partial density of states (PDOS) of the G/Si interfaces for (a) G/*u*:Si-H, (b) G/*u*:Si-2×1t and (c) G/*u*:Si-4×4t. The Fermi level is set at $E = 0$ eV. Black lines present total PDOS. Red, yellow, blue, and green lines present PDOS of the Si[4th] layer, Si[1st] layer, graphene on the substrates, and isolated graphene, respectively.
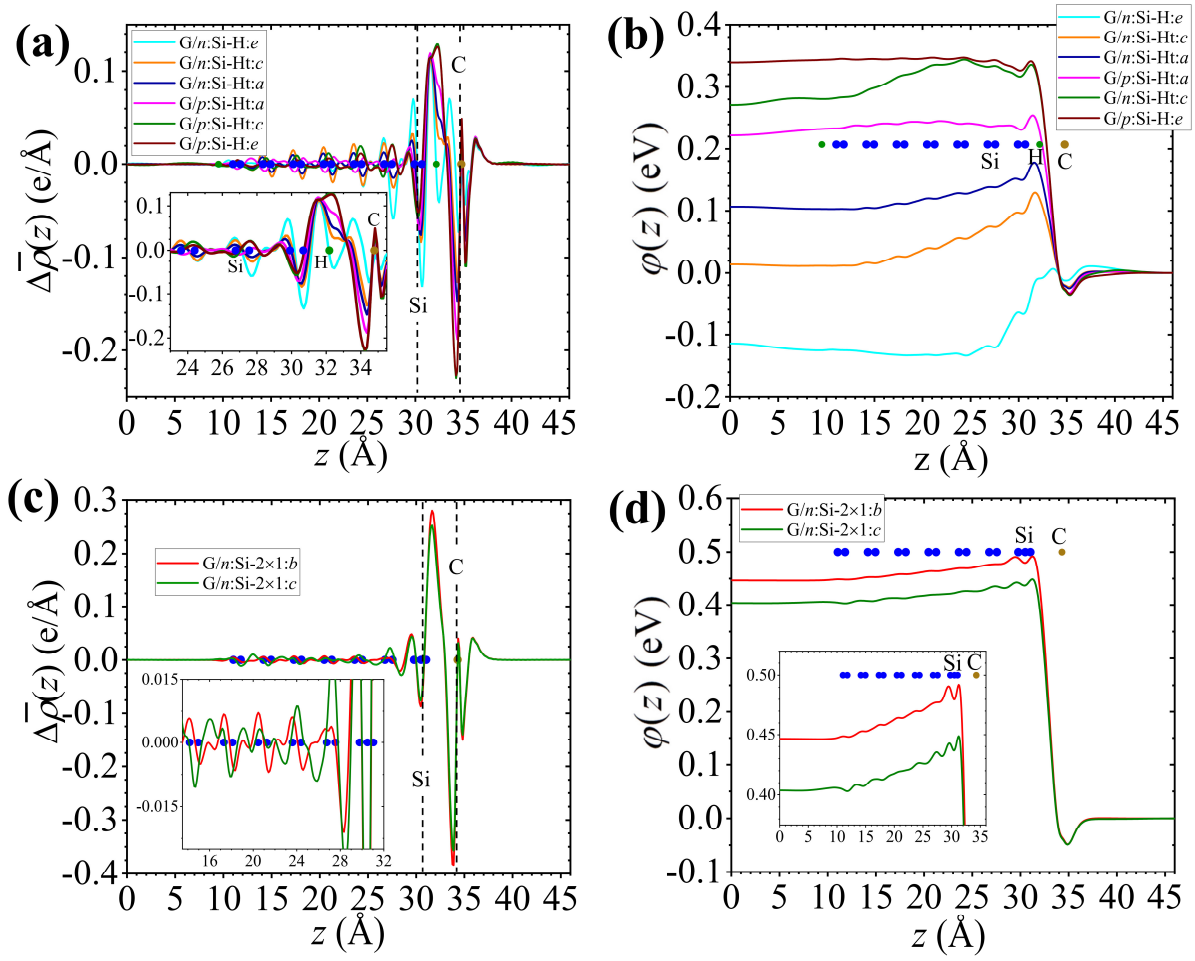
Figure S4. Plane averaged charge density difference, $\Delta\overline{\rho}(z)$, and interface-induced potential distribution, $\varphi(z)$, along the vertical z direction normal to the interfaces, respectively, for (a) and (b) the G/Si-H(t) interfaces; (c) and (d) the G/Si-2×1 interfaces. The inset plot shows a zoomed-in view of the main plot.
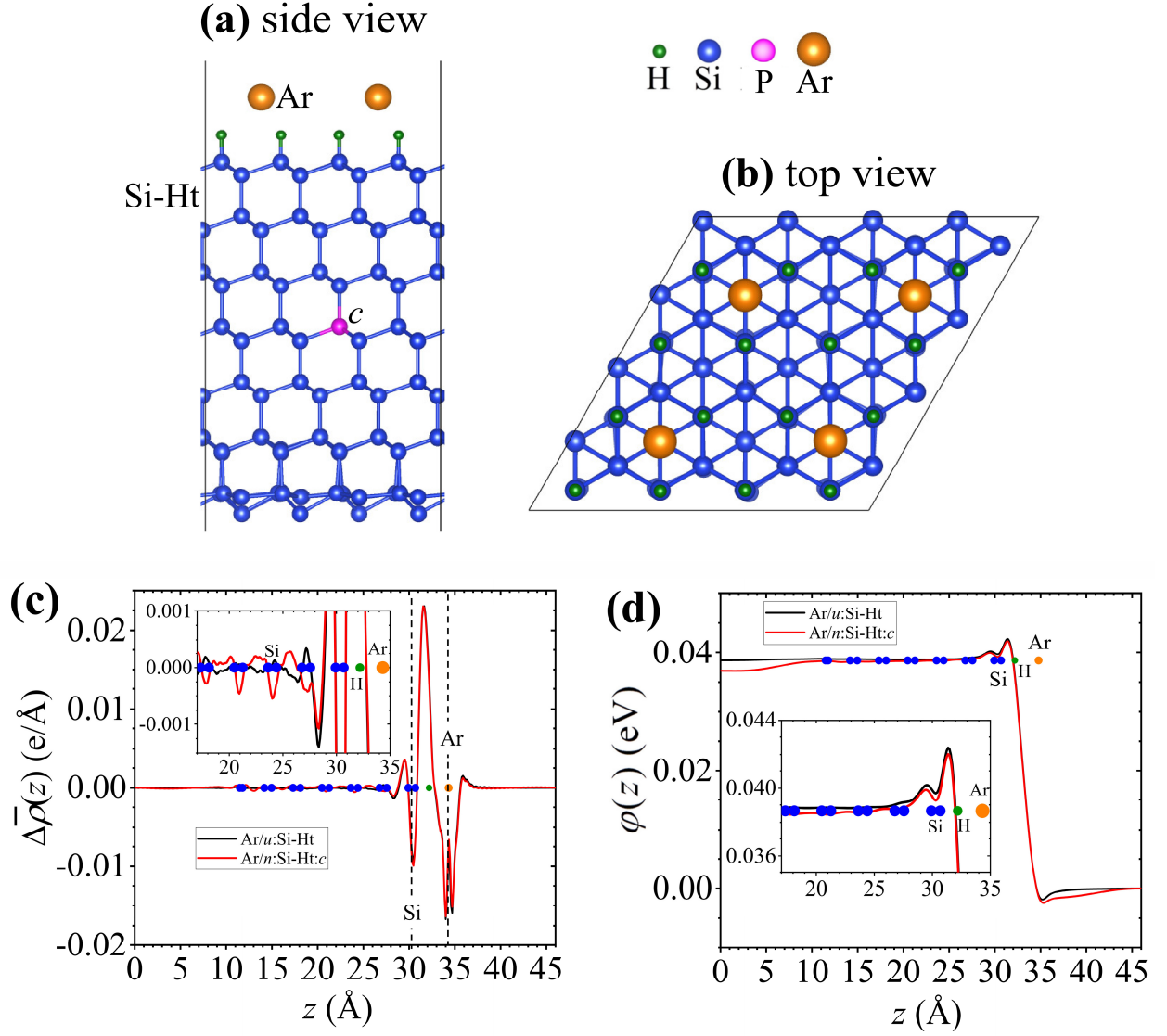
Figure S5. (a) Side view and (b) Top view of the Ar/(*u*,*n*):Si-Ht:(*c*) interfaces. The small green, middle blue and pink spheres are H, Si and P atoms, respectively. The large yellow ball is Ar atom. The P dopant atom is at *c* site of the Si-Ht substrate. (c) Plane averaged charge density difference, $\Delta\bar{\rho}(z)$, and (d) interface-induced potential distribution, $\varphi(z)$, along the vertical z direction normal to the Ar/*u*:Si-Ht and Ar/*n*:Si-Ht:*c* interfaces. The inset plot shows a zoomed-in view of the main plot.

Table S1. Calculated DFT results based on LDA and PBE functionals for the G/Si interfaces. Lattice mismatch, $\delta = (a_{Si} - a_{G})/a_{Si}$ (%), where a_{Si} and a_{G} are lattice constants of the Si substrate and isolated graphene, respectively; equilibrium interaction distance (d_{eq}), and binding energy per C atom (E_b) of the G/u:Si-2×1t and G/u:Si-4×4t interfaces.

Interfaces	δ (%)	d_{eq} (Å)	E_b (meV)
	LDA		
G/u:Si-2×1t	-0.132	3.221	16.9
G/u:Si-4×4t	-0.132	3.142	13.2
	PBE		
G/u:Si-2×1t	0.237	3.922	1.0
G/u:Si-4×4t	0.237	3.925	5.5

Table S2. Calculated values obtained using optB86b-vdW correction for the G/Si-H(t) and G/Si-2×1 interfaces. Electron affinity of Si substrate (χ_{Si}), work function of top Si surface (W_{Si}), work function of graphene-covered Si surface ($W_{G/Si}$), electron Schottky barrier height ($\Phi_n^* = E_c - E_F$), where E_c and E_F are the conduction band minimum energy of the substrate and the Fermi level, respectively; Fermi level shift in graphene (ΔE_F), and interfacial potential step ΔV.

Interfaces	χ_{Si} (eV)	W_{Si} (eV)	$W_{G/Si}$ (eV)	Φ_n^* (eV)	ΔE_F (eV)	ΔV (eV)
G/*n*:Si-Ht:*a*	3.983	4.51	4.40	0.54	0.014	0.15
G/*n*:Si-Ht:*c*	3.971	4.20	4.18	0.24	0.237	0.10
G/*n*:Si-H:*e*	4.005	3.94	4.07	-0.05	0.352	-0.07
G/*p*:Si-H:*e*	4.155	5.07	4.71	0.91	-0.295	0.33
G/*p*:Si-Ht:*c*	4.062	4.90	4.55	0.86	-0.138	0.32
G/*p*:Si-Ht:*a*	4.045	4.75	4.44	0.70	-0.020	0.23
G/*n*:Si-2×1:*b*	4.176	4.78	4.33	0.62	0.117	0.48
G/*n*:Si-2×1:*c*	4.179	4.69	4.25	0.51	0.199	0.44