Valence Band Control of Metal Silicide Films via Stoichiometry

Frank Streller,† Yubo Qi,‡ Jing Yang,† Filippo Mangolini,†,§ Andrew M. Rappe,†,‡ and Robert W. Carpick†,‡,¶

†Department of Materials Science and Engineering, ‡Makineni Theoretical Laboratories, Department of Chemistry, and ¶Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

**ABSTRACT:** The unique electronic and mechanical properties of metal silicide films render them interesting for advanced materials in plasmonic devices, batteries, field-emitters, thermoelectric devices, transistors, and nanoelectromechanical switches. However, enabling their use requires precisely controlling their electronic structure. Using platinum silicide (Pt$_x$Si) as a model silicide, we demonstrate that the electronic structure of Pt$_x$Si thin films (1 ≤ x ≤ 3) can be tuned between metallic and semimetallic by changing the stoichiometry. Increasing the silicon content in Pt$_x$Si decreases the carrier density according to valence band X-ray photoelectron spectroscopy and theoretical density of states (DOS) calculations. Among all Pt$_x$Si phases, Pt$_3$Si offers the highest DOS due to the modest shift of the Pt$_{3d}$ manifold away from the Fermi edge by only 0.5 eV compared to Pt, rendering it promising for applications. These results, demonstrating tunability of the electronic structure of thin metal silicide films, suggest that metal silicides can be designed to achieve application-specific electronic properties.

Metal silicide (Me$_x$Si) thin films were extensively studied in the 1980s and have found use in the microelectronics industry as materials for electronic contacts, local interconnects, and diffusion barriers. Recently, Me$_x$Si regained scientific attention as they are considered candidate materials for a variety of novel applications, such as plasmonics, lithium-ion batteries, field emitters, thermoelectric devices, semiconductors, and field-effect transistors. The increasing popularity of Me$_x$Si is a consequence of their metal-like electrical properties, semiconductor-like thermal transport, mechanical robustness, and thermal stability. However, Boltasseva et al. and Cheng et al. among others, pointed out that the composition and properties of Me$_x$Si need to be carefully optimized to fully utilize their potential in next-generation applications. We recently presented a methodology to precisely tune the composition of Me$_x$Si thin films by means of controlled solid-state diffusion. This allows for the formation of platinum silicide (Pt$_x$Si) thin films over a wide composition range (1 ≤ x ≤ 3), including the novel Pt$_x$Si stoichiometry, with an associated wide range of mechanical and electronic properties. While it is known that the Me$_x$Si composition strongly affects the resulting electrical, mechanical, and adhesive properties, systematic studies determining the effect of Me$_x$Si composition on specific properties are lacking. Here, we compare valence band (VB) X-ray photoelectron spectroscopy (XPS) measurements with calculations of the density of states (DOS) around the Fermi edge to elucidate the relationship between composition and electronic structure/properties for Pt$_x$Si thin films.

Using source-limited solid-state diffusion (i.e., films are formed by annealing of sequentially deposited Pt and a-Si thin films of specific thickness ratios), we fabricated Pt$_x$Si thin films of Pt$_2$Si, Pt$_x$Si, and PtSi. These films were interrogated using high-resolution VB XPS measurements to determine the DOS at the Fermi edge, which accurately determines the electronic structure and many of the electronic properties of these Pt$_x$Si films. A high DOS at the Fermi edge is a requirement for having high electrical conductivity. The Fermi edge shape therefore provides an indication of the electronic character of the tested material (metal, semimetal, or semiconductor), as shown schematically in Figure 1a. Metals are characterized by a large quantity of charge carriers (high DOS) near the Fermi edge that allows them to be efficient electrical conductors. Semimetals possess a significantly reduced DOS at the Fermi edge without an energy band gap (which, combined with their typically higher Seebeck coefficient and lower thermal conductivities compared to metals, makes them suitable thermoelectric materials). The Fermi edges of semiconductors are located inside of the band gap without any electronic states at the edge. Because XPS probes the occupied states of a material (see Figure 1b), the spectral features of a VB XPS spectrum directly correlate with the DOS. This relationship allows us to directly compare XPS measurements with theoretical DOS calculations.

Figure 2 shows the results of the VB XPS measurements and the theoretical DOS calculations for [Pt], [Pt$_2$Si], [Pt$_3$Si], and [PtSi] films (the “…” notation refers to the dominant phase of four respective mixtures achieved experimentally, as shown in Figure 2c). The composition of the produced Pt$_x$Si films was determined using quantitative XPS (see the Experimental and Computational Details section). This demonstrated the phase selectivity as shown in Figure 2c; the [Pt$_3$Si] film was 74%
Pt$_3$Si, the [Pt$_3$Si] film was 70% Pt$_3$Si, the [PtSi] film was 92% PtSi, and the [Pt] film was 100% Pt. These exact compositions were also employed in the theoretical DOS calculations using a linear combination approach to ensure a better comparability of the results. The VB XPS measurements show a direct correlation between the Si concentration and the Fermi edge shape (Figure 2a). This agrees with recent work by Fryer and Lad, who performed VB XPS measurements of co-deposited Pt$_x$Si films (1 ≤ x ≤ 3). The experimental DOS at the Fermi edge systematically decreases with increasing Si content of the silicide. The dotted vertical lines represent the location of the Pt$_{5d}$ manifold for PtSi (2.7 eV below the Fermi edge), Pt$_2$Si (1.8 eV below the Fermi edge), and Pt$_3$Si (0.5 eV below the Fermi edge). (c) Thin film composition of [Pt], [Pt$_3$Si], [Pt$_2$Si], and [PtSi] samples as determined from quantitative XPS measurements.

Figure 2 shows a direct comparison of the experimental and theoretical Fermi edge shapes and compositions for [Pt], [Pt$_3$Si], [Pt$_2$Si], and [PtSi] samples. (a) Experimental Fermi edge shapes of [Pt], [Pt$_3$Si], [Pt$_2$Si], and [PtSi] samples. The VB electron population decreases with increasing Si content of the silicide. (b) Theoretical Fermi edge shapes of [Pt], [Pt$_3$Si], [Pt$_2$Si], and [PtSi] samples. The VB electron population decreases with increasing Si content of the silicide. (c) Thin film composition of [Pt], [Pt$_3$Si], [Pt$_2$Si], and [PtSi] samples as determined from quantitative XPS measurements.

Pt$_3$Si, the [Pt$_3$Si] film was 70% Pt$_3$Si, the [PtSi] film was 92% PtSi, and the [Pt] film was 100% Pt. These exact compositions were also employed in the theoretical DOS calculations using a linear combination approach to ensure a better comparability of the results. The VB XPS measurements show a direct correlation between the Si concentration and the Fermi edge shape (Figure 2a). This agrees with recent work by Fryer and Lad, who performed VB XPS measurements of co-deposited Pt$_x$Si films (1 ≤ x ≤ 3). The experimental DOS at the Fermi edge systematically decreases with increasing Si concentration from Pt toward PtSi. The analyzed films show metallic and reduced-metallic Fermi edge shapes in the case of Pt and Pt$_3$Si, respectively, and typical semimetallic behavior for the Pt$_2$Si and PtSi films. The theoretical DOS calculations show a similar reduction of the DOS at the Fermi edge from Pt to PtSi. Additionally, the calculated DOS for Pt, Pt$_3$Si, and PtSi are similar to those reported in previous works by Bentmann et al. and Franco et al. No DOS calculations for Pt$_3$Si have been previously reported in the literature.

Figure 3 shows a direct comparison of the experimental and theoretical Fermi edge shapes and compositions for [Pt], [Pt$_3$Si], [Pt$_2$Si], and [PtSi] films. Overall, we find that all experimental Pt$_x$Si VB spectra capture not only the general shape but also several individual features of the theoretical Pt$_x$Si DOS very well (Figure 3b–d). However, Figure 3a shows that the experimental Pt VB spectrum is unable to resemble the structural detail of the theoretical Pt DOS. Comparisons of our XPS with other XPS data show excellent agreement, similarly, comparisons of our...
the theoretical DOS and other DOS calculations show excellent agreement, but there is some disagreement between the two for the case of Pt. This points toward an inherent difficulty in matching the VB XPS spectrum of Pt to its theoretical DOS counterpart. The reasons for this phenomenon are discussed by Goldmann et al. and Hofmann et al. The intensity and shape of XPS VB spectra of open d shell metals, such as Pt, are modified and therefore unable to resemble DOS calculations due to (1) instrumental resolution of the XPS system, (2) matrix element modulation across the width of the d band, (3) the lifetime of the photohole, (4) interaction of the photohole with the conduction electrons, and (5) inelastic electron scattering. The factor that most prominently influences the structural detail of the VB spectra is the lifetime of the photohole, which leads to a broadening of the XPS peaks. These effects are less pronounced in PtSi due to the filling up of the d shell due to silicidation, in agreement with our results.

The measured and calculated VBs for Pt and the PtSi films are dominated by the PtSi manifold. The PtSi position within the VB greatly influences the observed Fermi edge shapes and consequently the carrier densities. A maximum of the PtSi manifold is located directly at the Fermi edge in the case of Pt (Figure 3a), whereas it shifts further away from the Fermi edge for PtSi with increasing Si content. Our calculations show that the PtSi manifold of PtSi is shifted to approximately 2.7 eV below the Fermi edge, whereas the PtSi manifold of PtSi is only shifted to approximately 1.8 eV below the Fermi edge (see the dotted vertical lines in Figure 2b), similar to previously reported values. The novel PtSi films show a shift of the PtSi manifold of only approximately 0.5 eV, which results in a metallic-like character of the Fermi edge.

Table 1 quantitatively compares the experimental and calculated DOS of Pt, Pt3Si, Pt2Si, and PtSi by means of their normalized carrier densities. The carrier densities were obtained by integrating the experimental and theoretical DOS within a 2kBT (∼0.05 eV for T = 300 K) energy window around the Fermi edge. The normalized carrier densities computed from the VB XPS measurements are in excellent agreement with the DOS calculations and confirm the systematic decrease in carrier density with increasing Si content. The PtSi and Pt2Si films were found to possess approximately 17−19% and 20−28% of the carrier density of Pt, respectively. These values are in good agreement with theoretical calculations performed by Bentmann et al. The Pt-rich Pt3Si film possesses a very high carrier density of 59−61% of the DOS of Pt, which is a more than 3-fold improvement over the PtSi carrier density.
As mentioned above, a high DOS at the Fermi level is one of the requirements for having a high electrical conductivity. We performed four point probe measurements on the Pt, Pt$_3$Si, Pt$_2$Si, and PtSi films to determine the sheet resistance as an inverse measure of the electrical conductivity (Figure 4). The measured sheet resistance values show a systematic decrease in electrical conductivity from Pt to PtSi, which confirms the expected qualitative trend of the carrier density. The sheet resistance values for Pt, Pt$_3$Si, Pt$_2$Si, and PtSi were measured to be 2.6, 18.9, 31.8, and 57.6 $\Omega/\square$, respectively. The corresponding resistivity values were calculated to be 10.6, 75.5, 127.2, and 230.4 $\mu\Omega$−cm, respectively. The obtained sheet resistance and resistivity values for Pt, Pt$_3$Si, and PtSi are in good agreement with results reported in other works.\(^{26,27}\)

The high electrical conductivity (and, correspondingly, the low sheet resistance and resistivity) of Pt$_3$Si compared to that of Pt$_2$Si and PtSi could motivate the use of Pt$_3$Si in several applications as a replacement for Pt$_2$Si or PtSi. Most notably for the semiconductor industry, where PtSi is considered as an attractive material due to its high thermal stability. However, Pt$_3$Si suffers from low electrical conductivity due to its low DOS, which this work has verified. Recent work by Slepkov and Demkov investigates Ti doping of PtSi in an attempt to increase its DOS and thereby its electrical conductivity.\(^{31}\) The researchers succeeded in increasing the DOS of PtSi by approximately 1.7 times through alloying with 12.5 atom % Ti. However, while the Ti doping increased the DOS, it also introduced Ti impurities that act as scattering centers and decrease the electrical conductivity. Hence no doping is necessary to achieve this high DOS, Pt$_3$Si does not suffer from additional creation of scattering centers.

In summary, we show that the electronic structure and properties of Pt$_3$Si thin films can be tuned for specific applications between metallic and semimetallic properties by controlling the film stoichiometry. The comparison of VB XPS spectra with theoretical density functional theory (DFT) calculations shows that the DOS near the Fermi edge of Pt$_3$Si is significantly higher than that of Pt$_2$Si and PtSi. The resulting high electrical conductivity of Pt$_3$Si makes this stoichiometry particularly interesting for applications that demand high electrical conductivity combined with high thermal and mechanical stability.\(^{32}\) This work on Pt$_3$Si provides a framework for studying the tunability of the electrical properties of other metal silicides based on Ni, Cu, Au, Fe, Co, Pd, Ag, and Rh among others. We expect that the open d shell metals (e.g., Fe, Co, Pd) will exhibit the strongest tunability of the electrical properties due to their similarity with Pt, which was shown to have a strong compositional dependence on the Pt$_{3d}$ manifold position.

### EXPERIMENTAL AND COMPUTATIONAL DETAILS

**Thin Film Formation.** To form the Pt$_3$Si films, Pt and a-Si films were sputter-deposited in a Denton Vacuum Explorer 14 sputterer (Denton Vacuum Inc., Moorestown, NJ) with a purity of 99.999% for both films and subsequently annealed under high vacuum (10$^{-7}$ Torr) at 600 °C for a hold time of 10 min (reached after using a heating rate of 30 °C/min). Pt was deposited in dc mode at 450 W and a-Si in ac mode at 230 W. The thicknesses of the Pt and a-Si films were chosen to obtain near pure phases of Pt$_3$Si, Pt$_2$Si, and PtSi upon annealing.\(^{15}\) The Pt and a-Si depositions were conducted sequentially in the same deposition system under maintained vacuum. This minimizes contaminant adsorption between the layers and oxidation of the a-Si, both of which are inhibiting factors for silicidation. The Pt$_3$Si film thicknesses were between 40 and 50 nm for all films studied here.

**XPS Analysis.** The chemistry of the near-surface region was investigated by XPS using a customized XPS spectrometer (VG Scienta AB, Uppsala, Sweden).\(^{23}\) XPS analyses were performed using a monochromatic Al K$\alpha$ source (photon energy of 1486.6 eV). The residual pressure in the analysis chamber was consistently less than 1×10$^{-9}$ Torr. The spectrometer was calibrated according to ISO 15472:2001 with an accuracy of ±0.05 eV. Survey and high-resolution spectra were acquired in constant analyzer energy mode with pass energies of 200 and 100 eV, respectively. The full width at half-maximum (fwhm) of the peak height for the high-resolution Ag 3d$_{5/2}$ signal of a sputter-cleaned Ag sample was 0.57 eV. The spectra were processed using CasaXPS software (v.2.3.16, Casa Software Ltd., Wilmslow, Cheshire, U.K.).

**Background subtraction** was performed using the Shirley−Sherwood method. The quantitative evaluation of XPS data, as described in ref 29, was based on integrated intensity using a first-principles model and applying Powell’s equation. The inelastic mean free path was calculated using the TPP-2M formula.\(^{30}\) Curve synthesis for the Pt 4f peaks was performed by constraining the integrated intensity ratio of these two signals to 3:4 and their energy separation to 3.33 eV. The reference energies for Pt 4f$_{7/2}$ peaks were 71.05, 71.55, 72.18, and 72.75 eV for Pt, Pt$_3$Si, Pt$_2$Si, and PtSi, respectively, and are in agreement with literature values.\(^{12,15}\) The Pt 4f peaks have been chosen to determine sample surface chemistry due to their high intensity and the high sensitivity of their position to the Pt$_3$Si stoichiometry, in contrast with the less intense and less stoichiometrically sensitive position of the Si 2p peaks.

**Theoretical DOS Calculations.** DFT calculations were performed on Pt$_3$Si, Pt$_2$Si, Pt$_3$Si, and Pt with generalized gradient approximation (GGA) exchange−correlation functionals implemented in QUANTUM ESPRESSO package.\(^{32}\) We used norm-conserving plane-wave pseudopotentials for all of the species.\(^{33,34}\) The kinetic energy cutoff to the wave function expansion was $E_{\text{cut}} = 680$ eV. An 8 × 8 × 8 Monkhorst−Pack grid k−point mesh was used to sample the Brillouin zone (BZ) in structural optimization, while a denser one, 24 × 24 × 24, was used for DOS calculation. The

![Figure 4. Sheet resistance of [Pt], [Pt$_3$Si], [Pt$_2$Si], and [PtSi] samples.](Image)
occupation of the states around the Fermi energy $E_F$ was calculated from the Fermi–Dirac distribution\textsuperscript{36}

\[ f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \]

where $f(E)$ is the occupation probability for the state with energy $E$, $k$ is the Boltzmann constant, and $T$ is the temperature, which was selected to be 298 K. The exact experimental compositions, that is, as reported in Figure 2c, were employed in the DOS calculation to ensure better comparability. The DOS for a nonpure compound was estimated from a linear combination of the DOS of each of its components. Examples of DFT DOS calculations using a similar methodology can be found in refs 37–40.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: carpick@eas.upenn.edu. Phone: 205-898-4608.

**Present Address**

§F.M.: Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, LS2 9JT Leeds, United Kingdom.

**Author Contributions**

F.S. prepared the samples and carried out the XPS experiments and resistivity measurements. Y.Q. and J.Y. performed the DOS calculations. A.M.R. oversaw the DOS calculations. F.M. and resistivity measurements. Y.Q. and J.Y. performed the DOS calculations. F.M. prepared the samples and carried out the XPS experiments and resistivity measurements. Y.Q. and J.Y. performed the DOS calculations. A.M.R. oversaw the DOS calculations. F.S. edited the manuscript.

**Notes**

The authors declare no competing financial interest.

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