Synthesis and thermal stability of Pt₃Si, Pt₂Si, and PtSi films grown by e-beam co-evaporation

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Abstract

Platinum silicide thin films formed via solid–solid reaction of Pt–Si interfaces play an important role as interconnects in microelectronics. This “self-aligned” silicide formation, however, is diffusion-limited and only Pt₂Si and PtSi phases form. Also, their usefulness in electronic applications at high temperatures is limited due to agglomeration effects. Here, e-beam co-evaporation is presented as a means of fabricating well-defined films of Pt₃Si as well as the Pt₂Si and PtSi phases familiar to conventional, self-aligned silicide technology. Pt–Si films with a range of compositions (silicon atomic fractions of $X_{\text{Si}}=0.00\text{--}0.77$) were grown on r-sapphire substrates by co-deposition of independently controlled Pt and Si evaporant fluxes at 400 °C. Phase, morphology, and electronic properties were analyzed upon deposition and after vacuum annealing for 48 h at 1000 °C. As-deposited films with $X_{\text{Si}}<0.70$ are polycrystalline and at higher Si concentrations are fully amorphous. Valence spectra from Pt, Pt₂Si, and PtSi films confirm previous reports and a valence spectrum is presented for the stoichiometric Pt₃Si phase; these data provide experimental support for

recently proposed revisions to the standard transition metal–silicon bonding model. As-deposited films, nominally 200 nm thick, are electrically conductive in the range 0.1– 4.0×10^6 S/m and remain so after vacuum annealing for 48 h at 1000 °C. The phase, morphological, and electrical stabilities are attributed to the finely grained as-deposited morphologies of co-evaporated Pt silicide films, which hinder agglomeration at 1000 °C for much greater times than do morphologies of traditional, self-aligned silicides grown via solid-state reaction.

Keywords: electrode materials, vapour deposition, thin films, transition metal alloys and compounds, thermal analysis, X-ray and UV spectroscopies

1. Introduction

Solid-state reacted transition metal silicides serve many critical roles in silicon-based microelectronics (e.g., as interconnects) but the continued miniaturization of integrated circuits (ICs) puts many new demands on silicide materials. The interesting properties of PtSi include an exceptionally low Schottky barrier height on *p*-type Si (0.28 eV) [1], and although its electrical conductivity is only about half that of the more common TiSi₂ [2], the film conductivity is preserved at linewidths as narrow as 0.15 μm, while that of TiSi₂ critically diminishes below 0.50 μm [3,4]. Furthermore, Pt silicides have a relatively robust thermal and chemical stability [5] and low formation temperatures [6], which make them attractive for next-generation devices, given the high temperatures found in the final stages of some device fabrication processes [2]. With continued interest in Pt–Si materials,

multiple recent revisions have been made to the Pt–Si binary phase diagram [7–11] and to the electronic structure and bonding models of the PtSi and Pt₂Si phases [12–17].

The ability to grow silicide films with well-defined metal–Si stoichiometry across the entire compositional range is an attractive feature of the e-beam co-deposition technique and it has many advantages over other silicide growth methods. Firstly, device miniaturization requires very shallow contact depths and it is widely recognized that this will not be achieved by traditional solid-state reacted, “self-aligned” techniques. Co-deposition of metal and Si has been suggested as a means of minimizing the consumption of substrate Si during metal silicide formation (silicidation), and this approach has been demonstrated for co-evaporated Pt silicides in a series of experiments by Eizenberg and Tu [18–20], in which Pt–Si films with X_{Si} ranging from 0.25 to 0.50 were co-deposited on *n*-type Si and annealed; the results indicated that contact depth can be directly controlled via deposited film compositions. Secondly, the tunability of film composition affords the deposition of Si-rich (off-stoichiometric) films in which the excess Si offers a safety margin during thermal oxidation, as has been demonstrated for co-sputtered Pt–Si thin films by Murarka et al. [21]. Finally, by co-depositing films with appropriate metal-to-Si ratios, crystalline phases that do not form during self-aligned silicide growth can be targeted; as is characteristic of diffusion-limited solid-state reactions, only a subset of all thermodynamically stable phases can kinetically form throughout the duration of the reaction. For example, only the Pt₂Si and PtSi phases form during self-aligned platinum silicide film growth [22–24] and other Pt–Si phases (e.g., Pt₃Si) develop only as minor phases during growth or subsequent processing [25–27]. Using co-evaporation, the mixing of Pt and Si species occurs locally during deposition, requiring much smaller diffusion lengths to achieve silicide formation.

Agglomeration (a.k.a. solid-state dewetting) plagues micro and nanoscale applications of thin films at elevated temperatures, where narrow electrode linewidths progress from continuous films to discontinuous island-type structures, thereby diminishing electrically conductive pathways. The thermodynamics of the solid-state dewetting of thin films has been extensively reviewed in Ref. [28] by C.V. Thompson. Film agglomeration is driven by solid-state surface self-diffusion, whereby material is transported away from grain boundaries in order to reduce gradients in the film curvature and minimize the free energy of the film–substrate interface. Grooving at a particular grain boundary will proceed until a sufficiently large hole has formed through the entire thickness of the film, after which capillary energies drive the retraction of its edge, furthering hole growth.

Thermodynamically, however, the greatest groove depth attainable at a particular grain boundary is functionally proportional to the radius of the grains. Hole nucleation is therefore suppressed for grain sizes below some critical grain radius [28]. For this reason, a smooth, finely grained film morphology should aid in the suppression of agglomeration; the high density of grain boundaries delays the rate of coarsening, which thereby limits grain boundary grooving and long-range material diffusion, and ultimately hinders agglomeration. Physical vapor co-deposited films generally have smoother surfaces and are more finely grained than films formed by solid-state reaction [29]. Thus, growth by electron beam co-evaporation is proposed as an approach to suppress agglomeration effects in Pt–Si thin films. Indeed, these films are shown herein to be morphologically stable at temperatures up to 1000 °C and for vacuum annealing times well beyond where solid-state reacted Pt silicides routinely agglomerate [21].

2. Experimental

Pt-Si thin films with various compositions ($X_{\text{Si}} = 0.00$ to 0.77) were grown on epitaxially polished r-sapphire substrates at $400\text{ }^{\circ}\text{C}$ by electron beam (e-beam) co-evaporation from independently controlled high purity Pt (99.99995%) and Si (99.999%) sources. Blanket film coverage of 200 nm thick Pt-Si samples were grown in a UHV deposition chamber with a base pressure $< 7 \times 10^{-8}$ Pa. Both evaporant fluxes were individually measured by quartz crystal monitors (QCMs) that were calibrated against film heights measured by surface profilometry. The evaporant fluxes both impinged at a 28° -angle relative to the sample normal and onto the centrally located sample holder (ca. 40 cm from the sources), which rotated at 0.1 Hz while heating the substrates at $400\text{ }^{\circ}\text{C}$. Following film deposition, samples were transferred *in vacuo* to an X-ray photoelectron spectroscopy (XPS) chamber for core-level (CL) and valence band (VB) analysis, measured at room-temperature using Al $K\alpha$ radiation and a SPECS hemispherical electron analyzer. Binding energy calibration of XPS data is accurate to ± 0.1 eV following a Fermi edge fitting procedure in the SpecsLab data acquisition software and corroboration with a sputter cleaned Au thin film.

The films were characterized in the as-deposited state as well as after various vacuum annealing times. Annealing of the films was performed using a graphite/PBN heater for up to 48 h at $1000\text{ }^{\circ}\text{C}$ with a $< 10^{-6}$ Pa background pressure in the UHV chamber. Film electrical conductivities were measured at room-temperature using a 4-point collinear probe and corrected according to film dimension ratios [30]; stylus profilometry was used to measure as-deposited film thicknesses. Room-temperature XRD spectra were acquired with a PANalytical X'Pert Pro Materials Research Diffractometer, using Cu $K\alpha$ radiation and line-focused single-bounce-mirror incident optics; θ - 2θ scans were taken with a 3° offset in ω to avoid the very intense $\{10\bar{1}2\}$ Bragg peaks from the r-sapphire substrate. A Zeiss

NVision 40 scanning electron microscope (SEM) was used in both secondary and backscattered electron imaging modes for qualitative characterization of the film surface morphologies. Also, energy dispersive X-ray spectroscopy (EDS) was used in tandem with SEM to characterize the elemental composition of select film features.

3. Results and Discussion

3.1 Composition and bonding

When comparing the silicon fraction of the Pt–Si evaporant flux ($\emptyset_{\text{Si}}$) as measured by the QCM with the compositional [atomic] silicon fraction (X_{Si}) of the correspondingly deposited film as determined by XPS, it was found that $X_{\text{Si}} \approx \emptyset_{\text{Si}}$, meaning that there exists a 1:1 sticking coefficient of Pt and Si fluxes on the r-cut sapphire substrate at 400 °C. Film compositions were quantified *in vacuo* after growth by analyzing XPS core-level intensities before the films were exposed to air. Due to the overlap of the Si 2*p* photopeaks with the strong Pt 4*f* plasmon-loss features, the Si 2*s* was used for quantifications. Whereas simple area integration above background is sufficient for the Si 2*s* photopeak, quantification of Pt requires fitting the data with theoretically modeled synthetic peaks.

Figure 1 displays an XPS spectrum from an as-deposited Pt silicide film with $X_{\text{Si}} = 0.31$. The inset plot contains a survey scan over the binding energy (BE) range that includes the Pt and Si photopeaks used for quantification, while the feature plot is a higher resolution narrow scan of the Pt 4*f*/5*p* region. The large photoionization cross-sections for the Pt 4*f* photopeaks (Relative Sensitivity Factors of 9.81 for Pt 4*f*_{7/2} and 1.04 for Si 2*s* with Al K α radiation [31]) results in prominent Pt 4*f* satellites arising from K α _{3,4} radiation in the Al X-ray source [32], which partly overlap the 4*f*_{7/2} photopeak. Moreover, the Pt 5*p*_{1/2} lies

between the $4f$ photopeak doublet and the ensemble of $4f$ satellites. Thus, the fitting of the Pt $5p_{1/2}$ peak was modeled after the more accessible $5p_{3/2}$ peak. For Pt–Si films, the asymmetry of the Pt photopeaks (and their satellites) (**Fig. 1**) is characteristic of the Doniach-Sunjić lineshape that is typical in photoemission spectra from metals, and it is increasingly intense with increasing metallic character [33,34]. Thus, to fit Pt photopeak areas for a diverse set of Pt:Si compositions, a tunably asymmetric Lorentzian lineshape [35] was used.

As shown in **Fig. 2**, the BE of the observed Pt $4f_{7/2}$ photopeak increases as the Si fraction, X_{Si} , increases from zero. For a film with $X_{\text{Si}} > 0.50$, the Pt $4f_{7/2}$ is chemically shifted by +1.46 eV compared to elemental Pt ($X_{\text{Si}} = 0.00$). A larger core-level shift for films between $X_{\text{Si}} = 0.00$ and $X_{\text{Si}} = 0.33$ compared to those between $X_{\text{Si}} = 0.33$ and $X_{\text{Si}} = 0.50$ is consistent with the chemical bonding in PtSi and Pt₂Si: the former consists of strong covalent Pt–Si bonds whereas the latter is comprised of much weaker covalent bonds and a greater number of Pt–Pt metallic bonds [16]. The Pt $4f_{7/2}$ BE for Pt, Pt₃Si, Pt₂Si, and PtSi are measured to be 70.9 eV, 71.5 eV, 72.1 eV, and 72.4 eV, respectively. These values for all four compositions are consistent with those reported elsewhere for Pt and the Pt silicides [36–43].

Figure 3 presents XPS valence band (VB) spectra measured from Pt–Si films of different compositions. Each data set was background-normalized in intensity and then vertically offset for comparison. Denoted on the left-hand side of the spectra are crystalline phases determined by XRD and Si atomic fractions quantified by XPS. The VB spectra measured from stoichiometric Pt, Pt₂Si, and PtSi films agree well with those reported in the literature

for bulk and thermally reacted film samples [15,16,37,44–46]. This work additionally presents a VB-XPS profile from a film consisting of a pure Pt₃Si phase.

According to the conventional VB model for *d*-metal silicides [37,47–51], the valence structure of Pt silicides has been believed to consist of the following four features: (i) a localized, nonbonding Pt 5*d* band surrounded by (ii) bonding and (iii) antibonding counterparts of Si 3*p*–Pt 5*d* hybridization, and finally, (iv) a high-BE feature that has been observed for every metal silicide and believed to be associated purely with the dehybridized Si 3*s* states that arise after silicidation disrupts the Si *sp*³ bond. Typical of *d*-metal silicides, the Fermi level intersects the density of 3*p*–5*d* antibonding states. Recently, studies by Franco et al. [15,16] and Klepeis et al. [14] suggest that the previously accepted model for bonding in the silicides, one of a simple transfer of charge from Si to Pt, where nonbonded Pt 5*d* orbitals are highly localized and Si 3*s* orbitals are similarly uninvolved with bonding, is not correct, at least for Pt₂Si and PtSi. Rather, a more complex bonding picture is proposed, in which a charge reconfiguration creates a mixture of metallic and covalent, 2-centered and 3-centered bonds [12,14] resulting in a shift of both parent atoms' CLs to higher BEs, relative to their elemental positions. Moreover, in this new model, Pt 5*d* and Si 3*p* mixing extends throughout the entire VB, and Si 3*s*, Si 3*d* and Pt 6*p* states also contribute, though to a lesser extent, to the bonding in Pt₂Si and PtSi [15,16].

Experimental support for this new model is found in **Fig. 3**. Three additional, subtle VB features were discovered and labeled by Franco et al. as α , β , and γ . These were each identified to be comprised predominantly of Pt 5*d* states, but with varying contributions from Pt 6*p*, Si 3*p*, and Si 3*s* orbitals. All three features were observed by Franco via

photoelectron and X-ray fluorescence spectroscopies and in local density approximation (LDA) theoretical calculations. The data shown in **Fig. 3** have revealed subtle features at the α , β , and γ positions in the VB-XPS data for the co-evaporated PtSi phase. When combined with the abovementioned peaks, *i* through *iv*, these additional features support the notion that the Pt 5*d* orbitals are not so localized, but rather extend throughout the VB.

The theoretical orbital-resolved partial density of states (PDOS) for PtSi reported by Bentmann et al. [12] is in good agreement with that of Franco et al., including these newly identified features. In addition, Bentmann found that the DOS of Pt₂Si also possesses an α -like feature of similar *d* and *p* character, as in PtSi, that is similarly positioned within the VB despite the bulk of the main *d* manifold shifting towards the Fermi level. This trend can be observed when comparing PtSi to Pt₂Si in the VB-XPS data of **Fig. 3**. Whether β or γ are present in the VB of Pt₂Si is unclear from Bentmann's calculation, and there is an absence of DOS studies in the literature for the Pt₃Si phase.

A clear broadening of the VB profile is observed as the Pt content increases, which is consistent with increasing *d*–*d* overlap of neighboring Pt atoms; similar *d*–*d* interactions are reported for the Au₂Al, AuAl, and AuAl₂ phases in Au–Al alloys [52–54]. Analogous to Au–Al compounds of increasing Au content, several trends are observed for increasingly Pt-rich Pt–Si thin films: an increase of intensity and broadening of *d* bands, due to a greater *d*–*d* interaction between neighboring Pt lattice sites, and an increase in intensity of the 5*d*–3*p* antibonding band (peak *iii*), accompanied by a shift of this peak, and the 5*d*–3*p* bonding peak (peak *ii*), toward Fermi level.

Peak *iv* is situated at the bottom of the PtSi VB. Franco and Bentmann have both shown that rather than consisting of pure Si 3s orbitals, the Pt 5d states contribute almost an equal amount to this peak. As predicted by the calculated PDOS of PtSi and Pt₂Si, peak *iv* moves to a greater BE for Pt₂Si (**Fig. 3**); this peak further shifts upward in BE for the Pt₃Si phase. The Si CL transitions exhibit 0.0 eV of shifting in BE between any of the three silicides, however VB peak *iv* shifts a total of 1.0 eV between PtSi and Pt₃Si. This is contrary to what would be expected if the Si 3s orbitals are instead spatially localized and, like CL orbitals, shift only due to potential energy effects involved in Pt–Si charge transfer. The fact that this peak shifts unlike the Si CLs and away from the main Pt 5d manifold is supporting evidence for a Pt–Si DOS model in which Pt 5d orbitals extend throughout the VB and the Si 3s states play a role in bonding.

3.2 Phase identification

For co-evaporated Pt–Si films with nominal Pt:Si ratios of 1:1, 2:1, and 3:1 (i.e., $X_{\text{Si}} = 0.50, 0.33, 0.25$), phases of PtSi, Pt₂Si, and Pt₃Si respectively form upon deposition at 400 °C, according to X-ray diffraction (XRD) (**Fig. 4**). The compositional (X_{Si}) ranges over which a particular Pt–Si phase exists is evident in **Fig. 5**, where the phases identified by XRD are plotted versus film compositions calculated from XPS. (The electrical conductivity data included in **Fig. 5** are discussed in Section 3.4.) As shown in **Fig. 5**, films deviating ± 5 at.% Si from PtSi, Pt₂Si, and Pt₃Si stoichiometries still exhibit single-phase silicide XRD spectra (hereafter referred to as “single-phase” films), like those displayed in **Fig. 4**, and for films exceeding these compositional ranges, a solid-solid mixture of two contiguous phases was observed in the XRD pattern. Pt–Si co-evaporation with very low Si content ($X_{\text{Si}} < 0.16$)

yields films with Pt grains coexisting with finely dispersed Pt₃Si nanocrystallites. Mixed films that contain Pt₃Si + Pt₂Si phases form over a very narrow range, as seen in **Fig. 5**; the formation enthalpies for these two phases (-12.3 and -14.0 kcal/mol, respectively [55]) appear to advocate the growth of mixed films in this compositional range.

No majority-silicon phases (e.g., Pt₂Si₃, Pt₄Si₉) were observed under any growth conditions, indicating that the elevated deposition temperature (400 °C) and relatively low total deposition rate (0.5 Å/s) are sufficient to prevent the nucleation of such metastable phases, which have elsewhere been induced via post-deposition laser irradiation [56] and ion-beam mixing [57-61]. For films deposited with $X_{\text{Si}} > 0.50$, the excess Si (not bound in PtSi) was found to be amorphous. The growth of amorphous Si (a-Si) films via e-beam deposition in vacuum (7×10^{-4} Pa) has been demonstrated by Fang et al. [62], and 520 °C was found to be the critical temperature below which fully amorphous films form on alumina substrates. Pt-Si films grown with $X_{\text{Si}} > 0.70$ (omitted from **Fig. 4**) are fully amorphous as-deposited with only a very broad peak extended over Bragg angles $2\theta = 15\text{--}35^\circ$.

Co-evaporated Pt-Si films with $X_{\text{Si}} < 0.65$ all exhibit polycrystalline XRD patterns with slightly preferred textures, as shown in **Fig. 4**. The expected cubic-Pt, monoclinic-Pt₃Si, tetragonal-Pt₂Si, and orthorhombic-PtSi phases were observed [63-66], and Scherrer analysis of several XRD peaks for each phase indicates that all Pt-Si film types have a nominal crystallite grain size of 15-30 nm perpendicular to the film, meaning that on average 7-13 crystalline grains make up the 200 nm film thickness.

For mixed, Pt + Pt₃Si films with overall compositions of $X_{\text{Si}} = 0.10$ to 0.15, 40-60% of the film is a Pt₃Si phase, and in this case the Pt grains become less (111) textured than a pure

Pt film and are more evenly distributed among (111), (200), and (311) orientations. For the stoichiometric Pt₃Si film composition, a small amount (ca. 5%) of β Pt₃Si is present (**Fig. 4**), which is the high-temperature, orthorhombic polymorph [67] of the Pt₃Si structure. The Pt-rich side of the Pt–Si binary phase diagram has undergone several revisions in recent decades and is still under some dispute [7]; one result of these revisions is that the polymorphic transition temperature for α Pt₃Si $\rightarrow$ β Pt₃Si, which was long reported as 360 °C [11], has recently been reported as 440 °C [7,8]. The presence of the secondary phase, β Pt₃Si, is observed here for depositions performed with a 400 ± 10 °C substrate temperature.

3.3 Film morphology

Scanning electron microscopy (SEM) was used to study film nanostructure, including morphological grain size and heterogeneity. **Figure 6** presents plan-view images from as-deposited films of stoichiometric Pt₃Si, Pt₂Si, and PtSi phases, as well as two dual-phase films: a Pt₂Si–PtSi film ($X_{\text{Si}} = 0.39$) and a Si-rich PtSi phase ($X_{\text{Si}} = 0.64$). For a single-phase PtSi film (**Fig. 6d**), the grains are about 3–5 times larger in diameter compared to the single-phase Pt₂Si film (**Fig. 6b**). For the mixed Pt₂Si–PtSi film (**Fig. 6c**), two distinct grain types are evident, which are similar to those found in the Pt₂Si and PtSi films; EDS measurements confirmed that the two different grain types are in fact those of Pt₂Si and PtSi.

The melting-point of Pt₃Si is lower than those for the other two silicides [7,8], which may be the cause of the morphology exhibited by single-phase Pt₃Si films (**Fig. 6a**) that is quite dissimilar to those of single-phase Pt₂Si and PtSi films. We speculate that the lateral non-

uniformity of Pt₃Si grains is the result of an Ostwald ripening-like mechanism between neighboring grains during film growth. It is also interesting to note the presence of 5–25 nm precipitates that decorate the Pt₃Si film surface. These particulates are identified by EDS and grazing-incidence XRD (GIXRD) as c-Pt nanoparticles and are observed to accumulate only at the growth surface and not beneath. Studies are underway to further probe the existence of these nanoparticles and the early stages of Pt₃Si grain ripening for other film thicknesses and deposition temperatures.

As observed in **Fig. 6e**, excess Si in the $X_{\text{Si}} = 0.64$ film appears to form an amorphous-Si matrix that coexists with crystalline PtSi grains. This amorphous phase was confirmed by EDS and CL-XPS to be pure Si and contain no significant amount of oxygen. Previous reports discuss similar accumulation of excess Si at the surfaces as well as at grain boundaries of Si-rich metal silicide films grown by co-sputtering [68–71].

3.4 Electrical conductivity

In **Fig. 5**, electrical conductivity data are presented for as-deposited Pt–Si thin films over the compositional range $0.00 \leq X_{\text{Si}} \leq 0.77$. Electrical resistance in thin films arises from several simultaneously operative electron scattering mechanisms, including background scattering within a single crystal grain (due to phonons and point defects) as well as scattering at the crystalline and morphological grain boundaries and external surfaces [72,73]. As a result, lower conductivity values are often found for thin films compared to bulk systems. In addition to defect and grain boundary scattering, excess a-Si that can collect in grain boundaries behaves like a capacitive dielectric in Si-rich silicides, increasing the boundary potentials, and thereby greatly decreasing film conductivity [68–71]. This

mechanism might explain the poor conductivity observed for Si-rich films ($X_{\text{Si}} > 0.60$), like that depicted in **Fig. 6e** and discussed in Section 3.3.

The electrical conductivities of the Pt silicide phases have values within a factor of two and are altogether two to three times less than that for films of pure Pt. As shown in **Fig. 5**, stoichiometric Pt_3Si , Pt_2Si , and PtSi films have room-temperature conductivities of $0.74 \pm 0.23 \text{ MS/m}$, $1.72 \pm 0.43 \text{ MS/m}$, and $1.02 \pm 0.48 \text{ MS/m}$, respectively. The values for Pt_2Si and PtSi are roughly half of those for Pt_2Si and PtSi films formed by solid-state reaction [6], which generally yields larger grain sizes compared to co-deposition [29]. On the other hand, the values are quite consistent with the conductivities of annealed Pt silicide films grown by co-sputtering [21].

The prominence of metal silicides in microelectronics has resulted in the prevalent use of solid-state reactions between metal films and Si substrates for silicide formation. As a result, there are few reports of synthesizing large regions of the Pt_3Si phase and reports on its electronic properties are accordingly scarce. Streller et al. [74,36] recently demonstrated that by replacing single crystalline (sc-) or polycrystalline (poly-) Si with a sputtered amorphous Si precursor film, solid-state silicide reaction of a bilayer of a-Si/Pt yields mixed-phase, sub-50 nm thick films that predominantly consist of a Pt_3Si phase. Si and Pt were sequentially sputtered in various Si:Pt thickness ratios onto PELCO 50 nm silicon nitride (Si_3N_4) support TEM grids and annealed to form mixed films either primarily consisting of Pt_3Si , Pt_2Si , or PtSi via source-limited (i.e., Si-limited) or kinetically limited (i.e., time/temperature-limited at fixed temperature/time) controlled solid-state diffusion. The authors reported that vital to the novel silicide formation sequence was their evidence

for Si being the diffusing species in Pt/a-Si reactions, unlike solid-state reactions of Pt on sc- or poly-Si substrates, such that Pt₃Si precedes the familiar formation series of Pt₂Si followed by PtSi. By conductive atomic force microscopy (C-AFM) using a Pt sputter-coated tip, they measured the contact resistance of PtSi films and Pt₃Si–Pt₂Si mixed films, compared to a Pt film, and determined that the mixed film of Pt-rich silicides is a more metallic contact material (i.e., more similar to Pt) than is PtSi. However, no measurements of electrical sheet conductivity were presented therein.

In the same manner as Streller, Gas et al. [55] demonstrated the growth of primarily-Pt₃Si films via reacting a source-limited Pt/Si bilayer with a respective thickness ratio of 300 nm/100 nm. The authors, however, made no mention of the crystalline structure or deposition temperature for the evaporated Si precursor. While measuring conductivity *in situ* while heating up to 650 °C, phases of Pt₂Si, Pt₁₂Si₅, and Pt₃Si were observed to form in sequence and each co-existed with unknown fractions of unreacted Pt, according to XRD and Rutherford backscattering (RBS) analysis. The respective conductivities of the three phases were estimated as 3.5 MS/m, 3.1 MS/m, and 1.9 ± 0.4 MS/m, respectively.

It should be noted that Streller et al. [36] described the PtSi phase as less metallic than a mixture of Pt₂Si and Pt₃Si phases, while Gas et al. [55] reported decreasing conductivity values with increasing Pt content, proceeding from Pt₂Si to Pt₃Si. The data displayed in **Fig. 5** could be consistent with these other reports as it suggests a slight local maximum in electrical conductivity for the Pt₂Si phase amid the surrounding Pt silicides.

3.5 Thermal stability

Co-evaporated Pt–Si films were annealed in vacuum at 1000 °C in order to explore the thermal stability of their crystalline phase, morphology, and electrical conductivity. In the literature, the onset of agglomeration in Pt₂Si and PtSi films has been attributed to the localized melting of Pt-rich regions. According to the bulk phase diagram [7,8], the Pt–Si system consists of three eutectic points, which separate the four congruent melting phases: Pt, Si, and the two most stable alloys, Pt₂Si and PtSi. The lowest melting temperature in the binary system (ca. 830 °C) is found at the Pt-rich eutectic situated at $X_{\text{Si}} = 0.23$. It is assumed that near 830 °C, melting of Pt₃Si-like regions produce spots of enhanced diffusion that serve as activation sites for film dewetting and lead to the decrease in film conductivities reportedly observed around 800–900 °C [21,75].

For the case of e-beam co-evaporated Pt–Si films, no local or global agglomeration is observed after annealing at 1000 °C for 48 h, independent of film composition. **Figure 7** displays SEM images, revealing the morphological continuity that is preserved for Pt₃Si, Pt₂Si, and PtSi films after the 48 h anneal. This stability is radically different than in the case of solid-state reacted Pt silicides [21,75–77] for which agglomeration routinely proceeds within 1 h at 850 °C in vacuum or inert atmospheres, causing rapid deterioration of film continuity. Because of the greater thermal stability of the co-evaporated film morphology, the sheet conductivities of these films remain stable to higher temperatures. Upon annealing all three of the co-evaporated silicides, the Scherrer grain sizes and conductivities alike increase only by 20–50%, with no apparent trends, characteristic of a reduction in the density of defects and/or grain boundaries. In the film with $X_{\text{Si}} = 0.64$, annealing results in only ca. 5% grain growth. Nonetheless, its conductivity increases by nearly 300% to a final value akin to that of the annealed PtSi films that were grown closer

to stoichiometry and without large quantities of excess a-Si. This result is most likely due to a redistribution of the a-Si away from grain boundaries during annealing and suggests that the a-Si phase indeed collects at grain boundaries, in addition to the exterior film surface, in as-deposited films.

The morphologies of the Pt₂Si and PtSi film are largely unaltered as a result of the vacuum annealing at 1000 °C; grain sizes and shapes are nearly identical to those in as-deposited films and little ripening of neighboring grains is observed (**Fig. 7**). However, the morphology of the Pt₃Si films, which consisted of a network of interconnected grains in the as-deposited state, becomes much more coarsely grained and noticeably smoother following the 1000 °C anneal. This morphological change may be the result of re-solidification after melting at ca. 900 °C [7,8], however there is no conclusive proof of this mechanism, and the film remains wetted to the epitaxially polished substrate. Although the 1000 °C annealing temperature is above the melting point predicted for Pt₃Si by the bulk Pt–Si phase diagram, the Pt₃Si films remain primarily monoclinic in phase after cooling, with a slight increase in the amount of the high-temperature, orthorhombic polymorph (β Pt₃Si). The fact that a crystalline Pt₃Si phase is fully retained after annealing at 1000 °C indicates that it, like Pt₂Si and PtSi, is not a metastable silicide phase as grown by e-beam co-evaporation.

Murarka et al. [21] also observed a Pt₃Si phase present in co-deposited Pt–Si films with $X_{\text{Si}} = 0.25$, which were grown by room-temperature dc magnetron sputtering onto poly-Si and SiO₂ substrates. However, unlike the co-evaporated films presented here, a transformation of the Pt₃Si phase to either PtSi or Pt₁₂Si₅ phases was observed (for films grown on poly-Si

and SiO₂, respectively) when these films were annealed at 400–900 °C in a forming gas mixture.

Co-evaporated, single-phase Pt₃Si films remain morphologically stable for at least 48 h at 1000 °C, which is important to note considering that regions of a Pt₃Si-like composition, present in as-deposited PtSi films as a result of film heterogeneities and composition fluctuations, are believed to be the cause of the rapid agglomeration observed for solid-state reacted films of PtSi above 850 °C, as mentioned above. We expect that this superior thermodynamic stability and the suppression of agglomeration effects are due to the smooth and finely grained as-deposited morphologies of e-beam co-evaporated Pt silicides, which hinder the long-range mass transport necessary for hole growth, as predicted by thermodynamic modeling [28].

4. Conclusions

Pt–Si thin films with Si atomic fractions ranging from $X_{\text{Si}} = 0.00$ –0.77 were grown at 400 °C onto r-sapphire substrates by UHV e-beam co-evaporation from independently controlled Pt and Si evaporant sources. As-deposited films and films annealed up to 1000 °C in vacuum were characterized with the purpose of exploring their phase, morphological, and electrical stability at temperatures where solid-state reacted Pt–Si films routinely agglomerate. The ability to grow single-phase Pt₃Si films via e-beam co-evaporation is demonstrated and, depending on the film composition, crystalline phases of cubic-Pt, monoclinic-Pt₃Si, tetragonal-Pt₂Si, and orthorhombic-PtSi were observed to form. Films with excess Si in the range of $X_{\text{Si}} = 0.50$ –0.65 contain an amorphous-Si phase that collects at the film surface and in grain boundaries, whereas films with $X_{\text{Si}} > 0.65$ are fully amorphous.

Valence band XPS spectra from Pt, Pt₂Si, and PtSi phases agree with previous reports and a valence spectrum is presented for the Pt₃Si phase. These spectra offer experimental support for recently proposed revisions to the standard transition metal–silicon bonding model. Film morphology of co-evaporated Pt silicides is highly dependent upon phase and differs for each of the three silicide phases. As-deposited films, nominally 200 nm thick, are electrically conductive in the range of $0.1\text{--}4.0\times 10^6$ S/m and conductivities measured from single-phase Pt, Pt₃Si, Pt₂Si, and PtSi films are 3.66 ± 0.20 MS/m, 0.74 ± 0.23 MS/m, 1.72 ± 0.43 MS/m, and 1.02 ± 0.48 MS/m, respectively, suggesting a local maximum in conductivity for the Pt₂Si phase among the Pt silicides, in agreement with other reports. Electrical conductivities slightly improve after vacuum annealing for 48 h at 1000 °C and all films, stoichiometric and otherwise, remain morphologically stable from agglomeration during the anneal. Grain coarsening is observed for Pt₃Si films as a result of vacuum annealing, though the morphologies of Pt₂Si and PtSi films are largely unaltered. Additionally, Pt₃Si films retain their as-deposited silicide phase after annealing at temperatures beyond its near-eutectic bulk melting point, indicating that the Pt₃Si phase is not metastable as grown by e-beam co-evaporation. Because of the superior thermal stability of the co-evaporated film morphology, the sheet conductivities of co-evaporated films remain stable to higher temperatures, offering the opportunity to use them in high-temperature electronic applications where enhanced film stability is desired.

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Fig. 1. (Color online) XPS data for a film with $X_{\text{Si}} = 0.31$. The survey scan (inset) shows photoemission from several Pt and Si orbitals including Pt $4f$ and Si $2s$, which are used for Pt:Si quantification (X_{Si}). The narrow scan presents the Pt $4f$ and $5p$ photopeaks, as well as the $4f$ satellites, and illustrates the need for individual fitting of overlapping peaks.

Fig. 2. (Color online) Binding energies of the Pt $4f_{7/2}$ photopeak for Pt-Si films with different compositions (X_{Si}). The $4f_{7/2}$ peak shifts to higher binding energy with increased inclusion of Si during film growth. Dotted lines project the $4f_{7/2}$ binding energy associated with Pt_3Si , Pt_2Si , and $PtSi$ stoichiometries (i.e., $X_{Si} = 0.25, 0.33$, and 0.50), measured to be 70.9 eV for pure Pt and 71.5 eV, 72.1 eV, and 72.4 eV for the respective silicides.

Fig. 3. (Color online) Valence band spectra measured by XPS from as-deposited films comprised of stoichiometric Pt₃Si, Pt₂Si, and PtSi (red lines) compounds as well as a Pt–Pt₃Si mixed film with $X_{Si} = 0.14$, a PtSi–Si mixed film with $X_{Si} = 0.64$, and a pure Pt film for reference (black lines). Binding energies for all spectra are measured relative to the Fermi level, E_F . Several spectral features, identified in previous studies (Refs. [15,16]), are labeled for comparison. (See text for details.)

Fig. 4. (Color online) XRD data from as-deposited stoichiometric monoclinic Pt₃Si, tetragonal Pt₂Si, and orthorhombic PtSi films grown at 400 $^\circ$ C. All spectra were measured using a 3 $^\circ$ offset in ω to avoid the very intense Bragg peaks from the r-sapphire substrate. Miller indices from powder diffraction files are labeled.

Fig. 5. (Color online) Electrical conductivity data from as-deposited Pt-Si thin films, $0.00 \leq X_{Si} \leq 0.77$. Datum markers indicate the Pt-Si phase of the corresponding film, according to XRD. The stoichiometric compositions for each of the four phases (i.e., $X_{Si} = 0.00, 0.25, 0.33$, and 0.50) are denoted on the bottom axis by vertical arrows.

Fig. 6. Secondary electron SEM images (110k $\times$ mag.) of as-deposited co-evaporated Pt-Si films grown at 400 $^{\circ}$ C: (a) Pt₃Si, (b) Pt₂Si, (c) Pt₂Si-PtSi, (d) PtSi, and (e) PtSi-Si.

Fig. 7. Secondary electron SEM images (55k $\times$ mag.) of stoichiometric (a) Pt₃Si, (b) Pt₂Si, and (c) PtSi films after vacuum annealing at 1000 °C for 48 h, revealing their preserved morphological continuity during high-temperature processing.