Room-temperature formation of Pt$_3$Si/Pt$_2$Si films on poly-Si substrates

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Abstract. We have observed a phenomenon of formation of a thin bilayer Pt$_3$Si/Pt$_2$Si film at room temperature on poly-Si substrates in the process of Pt magnetron sputtering and wet etching, obtained such a film and investigated its structure and phase composition. By direct X-ray photoelectron-spectroscopic measurements, we have verified our previous observation of the Pt$_3$Si layer formation between Pt and poly-Si films as a result of Pt magnetron sputtering at room temperature. This layer likely appears due to a high enough temperature of Pt ions in the magnetron plasma, sufficient for the chemical reaction of the silicide film formation on the Si surface. The Pt$_3$Si layer likely forms from the Pt–Pt$_3$Si layer (Pt$_{95}$Si$_{5}$), which arises under a Pt film during magnetron sputtering, as a result of Pt removal by wet etching.

1. Introduction

Platinum silicides have attracted attention of researchers for a number of decades due to their exceptional prospects in microelectronics and silicon-based microphotonics [1–3]. PtSi infrared detector arrays represented a qualitative breakthrough and opened a new era in the infrared imaging technology [4, 5]. Now Pt silicides are considered as metals for Schottky-barrier formation to poly-Si:P in thin-film diode bolometers [6, 7]. There is no doubt about the prospects of their application as ohmic contacts and submicron lines in microelectronics especially taking into account their low formation temperatures that is very important for CMOS and especially for nano electronic devices [8–10]. In addition, low-temperature silicides, e.g. Pt$_3$Si, are expected to be suitable for formation of uniform Schottky contacts in devices of power electronics in which the sizes of contacts reach millimeters and nonuniformity of the barrier height causes a significant increase in reverse current [11]. Pt silicide ohmic contacts as well as Schottky barrier formation on polycrystalline [12] or amorphous silicon is of special interest for photovoltaic and sensor technology [7]. So, this class of materials should be considered as one of the friendliest ones to silicon technology. However, as the used silicide films become thinner and reach tens or even units of nanometers, their resistivity becomes of primary importance. In this connection, Pt$_3$Si, which has the lowest sheet resistance among the Pt silicides (18.9 $\Omega/\square$ in comparison with 2.6 $\Omega/\square$ of Pt, 31.8 $\Omega/\square$ of Pt$_2$Si and 57.6 $\Omega/\square$ of PtSi) [13], starts to play the main role. So, the development of simple processes of formation of thin Pt$_3$Si films becomes more and more important.

This letter describes a phenomenon of formation of a thin bilayer Pt$_3$Si/Pt$_2$Si film at room temperature on a poly-Si substrate as a result of Pt magnetron sputtering and wet etching, which itself is of high scientific interest, and introduces a simple process of obtaining of such films.
obviously corresponds to Pt which may be attributed to Pt$_3$ fer different composition in which the inelastic scattering happens [20].

obtained after Pt removal (figure 2). Monotonic growth of signal is observed in the spectrum on the right (at the higher signal (figure 2) that did not allow us to obtain reliable data on its energy position.

electrons of Pt. This allows us to make a conclusion that the film containing Pt is overlaid by a layer 

Figure 1. STEM image of the as-deposited Pt/poly-Si structure shows a poly-Si layer (1), a layer of Pt (2) and an interfacial layer (3) consisting of a Pt$_{95}$Si$_3$ layer (Pt$_{19}$Si) on a layer of Pt$_2$Si [6].

2. Experimental Details

2.1. Samples

A 35-nm thick film of platinum was deposited by magnetron sputtering at room temperature on a 125-nm thick poly-Si:P layer formed on a Si$_3$N$_4$/SiO$_2$/Si(001) artificial substrate (figure 1). After deposition, platinum was removed by chemical etching in a warm aqueous solution of aqua regia (H$_2$O : HCl : HNO$_3$ [4 : 3 : 1]; the reaction is 3Pt + 18HCl + 4HNO$_3$ → 3H$_2$[PtCl$_6$] + 4NO↑ + 8H$_2$O). Details of the sample preparation process can be found in Ref. [6].

2.2. Equipment and techniques

The samples were studied by means of the X-ray photoelectron spectroscopy (XPS). The measurements were carried out using a Riber EA 150 cylindrical mirror electron energy analyzer [14] installed in an ultrahigh-vacuum chamber; the residual gas pressure in the chamber did not exceed 7 $\times$ 10$^{-7}$ Pa. Non-monochromatic Al K$_\alpha$ X-rays ($\hbar\omega = 1486.7$ eV) were used for photoexcitation of electrons. Survey spectra were scanned at a resolution (FWHM) better than 1.8 eV; high resolution spectra of specific elements were obtained at a resolution not worse than 0.96 eV. XPSPEAK 4.1 peak fitting program was utilized for treatment of spectra. It was taken into the account during peak deconvolution that the Al K$_\alpha$ band consists of two lines, K$_{a1}$ and K$_{a2}$, with an energy difference of $\hbar\Delta\omega = 0.5$ eV. Shifts of peaks related to elements in chemical compounds were compared with the NIST X-ray Photoelectron Spectroscopy (XPS) Database [15, 16]. Relative concentrations of atoms were estimated from ratios of normalized areas under corresponding peaks. The inelastic mean free path (IMFP) was estimated using the TPP-2M equation and the NIST Database [17, 18]. The spectrometer was calibrated against the Si$^{+4}$ signal ($E_b = 103.6$ eV) since the C 1s XPS peak recorded at high resolution had a low signal-to-noise ratio (figure 2) that did not allow us to obtain reliable data on its energy position.

The scanning transmission electron microscopy (STEM) image was obtained using a Carl Zeiss Libra-200 FE HR transmission electron microscope; the WSxM software was used for image processing [19].

3. Results and Discussion

Figure 1 demonstrates a STEM image of the as-deposited Pt/poly-Si structure. This structures was previously analyzed in details using STEM, X-ray diffraction and reflection, and XPS. It is composed of a poly-Si layer, a layer of Pt and an interfacial layer consisting of a Pt$_{95}$Si$_3$ layer formed on a layer of Pt$_2$Si [6]. This structure was subjected to wet etching to remove Pt.

Photoelectron peaks of Pt, Si, O and C are observed in the survey photoelectron spectrum of the film obtained after Pt removal (figure 2). Monotonic growth of signal is observed in the spectrum on the right (at the higher $E_b$ side) of the Pt 4$f$ doublet that is explained by inelastic scattering of the photoexcited 4$f$ electrons of Pt. This allows us to make a conclusion that the film containing Pt is overlaid by a layer of a different composition in which the inelastic scattering happens [20].

A high-resolution photoelectron spectrum of Pt 4$f$ consists of three components (figure 3 (a)). The first one is described by a doublet with $E_b = 71.5$ eV and a distance between peaks $\Delta E = 3.38$ eV which may be attributed to Pt$_{3}$Si [16, 21–23]; the next one, with $E_b = 72.1$ eV and $\Delta E = 3.38$ eV, obviously corresponds to Pt$_2$Si [16, 21–23]. The third component lays at higher energies ($E_b = 73.62$ eV,
Figure 2. Survey XPS spectrum of the Pt-silicide/poly-Si film. The insert demonstrates a magnified region around the Pt 4f and Si 2p peaks.

\[ \Delta E = 3.38 \text{ eV} \] and may be attributed to both platinum oxide PtO\(_x\) \((E_b = 72.8 \text{ to } 74.6 \text{ eV})\), likely PtO \((E_b = 73.8 \text{ eV} \ [16])\), and PtCl\(_2\) \((E_b = 73.6 \text{ eV} \ [16])\) or [Pt(NH\(_3\))\(_2\)(NO\(_2\))\(_2\)] (CAS Registry No. 14286023, \(E_b = 73.7 \text{ eV} \ [16]\)) which may arise as a result of Pt etching in the \textit{aqua regia} solution. The ratio of peak areas for Pt\(_3\)Si, Pt\(_2\)Si and PtO\(_x\) is 64 : 28 : 8.

The main contribution to the signal of silicon (figure 3 (b)) is made by Si\(^{4+}\) \((E_b = 103.6 \text{ eV})\) obviously related to silicon dioxide. In addition, a Si\(^{3+}\) peak can be detected by deconvolution which can be explained by superposition of photoelectron peaks related to Pt\(_3\)Si, Pt\(_2\)Si \((E_b = 102.6 \text{ eV})\) and SiO\(_x\) compounds having a broad range of binding energy values \((E_b = 100.4 \text{ to } 103.6 \text{ eV} \ [16]\)\). An estimate of contribution of Si atoms contained in Pt\(_3\)Si and Pt\(_2\)Si to this peak, made in assumption of uniformity of the upper film and taking into account empirical sensitivity factors of platinum and silicon, gives the value of \(\sim 16\%\).

Notice that an additional cycle of etching in the \textit{aqua regia} solution changed neither a ratio of the photoelectron peak intensities nor their energy positions.

It should be noted also that a small photoelectron peak at \(E_b = 99.5 \text{ eV}\) is also observed in the Si 2p spectrum; it corresponds to pure Si of the polycrystalline substrate that allows us to roughly estimate the thickness of the formed film by 3 to 5 values of the inelastic mean free path of electrons, i.e. by the value from 5 to 10 nm.

A more accurate estimation of the film thickness can be made from the ratio of areas under the Pt 4f
Figure 3. (Color online) High-resolution XPS spectra of Pt 4f (a) and Si 2p (b) obtained from the resultant Pt silicide film on the poly-Si substrate; measured bands are shown by solid lines, peaks obtained as a result of deconvolution are drawn by dotted and dashed lines.

peaks of Pt$_3$Si and Pt$_2$Si $\sigma \approx 2.3$. Let us suppose that the Pt$_3$Si layer overlays the Pt$_2$Si one. This assumption is based on the X-ray phase analysis according to which the Pt$_2$Si and Pt$_{95}$Si$_{5}$ layers, 5.6 and 10 nm thick, respectively, arise between poly-Si and Pt as a result of Pt sputtering [6]. Considering the IMFP value [18] of Pt$_3$Si, we obtain the thickness of the Pt$_3$Si layer $h_1$ from the values of densities and molar weights of Pt$_3$Si and Pt$_2$Si, $\sigma$ and the thickness of the Pt$_2$Si layer $h_2$: $h_1 \approx 2.6$ nm. (The value
of $h_1$ is calculated from a recursive equation: $h_1 = h_\text{IMFP} \times \ln[2\sigma_{\mu_{PtSi}}\rho_{PtSi}h_3/3\sigma_{\mu_{PtSi}}\rho_{PtSi}h_1]$, where $h_\text{IMFP}$ is the inelastic mean free path of electrons in $\text{Pt}_3\text{Si}$ [18], $\sigma_{\mu_{PtSi}}$, $\rho_{PtSi}$, $\sigma_{\mu_{PtSi}}$, and $\rho_{PtSi}$ are molar weights and densities of $\text{Pt}_2\text{Si}$ and $\text{Pt}_3\text{Si}$, respectively.) So, the total thickness of the bilayer Pt-silicide film $h_1 + h_2 \approx 8.2$ nm that is in good agreement with the above rough estimate.

Now, if we assume that the $\text{Pt}_{95}\text{Si}_{15}$ layer previously detected under Pt [6] is a mixture of Pt and $\text{Pt}_3\text{Si}$ ($16\text{Pt} + \text{Pt}_3\text{Si}$) we may also suppose that Pt is etched away from this layer during processing in the \textit{aqua regia} solution and the $\text{Pt}_3\text{Si}$ layer is deposited atop $\text{Pt}_2\text{Si}$. We can estimate $h_1$ from the thickness of $\text{Pt}_{95}\text{Si}_{15}$ and the densities of Pt, $\text{Pt}_{95}\text{Si}_{15}$ ($20.5 \text{~g/cm}^3$) [6] and $\text{Pt}_3\text{Si}$: $h_1 \approx 2.4$ nm. Thus, the silicide film thickness estimate of 8.0 nm obtained from the X-ray phase analysis [6] corresponds with that obtained from XPS.

4. Conclusion

In summary, we can make the following conclusions.

(i) We have verified our previous observation of $\text{Pt}_2\text{Si}$ formation in between Pt and poly-Si films as a result of Pt magnetron sputtering at room temperature [6]. This phenomenon probably occurs due to high enough kinetic energy of Pt ions reaching the Si surface, sufficient to give rise to chemical reaction of the silicide film formation. It opens a pathway to room-temperature process of formation of thin Pt silicide films on Si.

(ii) We have discovered a phenomenon and proposed a way of formation of thin bilayer $\text{Pt}_3\text{Si}/\text{Pt}_2\text{Si}$ films on poly-Si substrates at room temperature by magnetron sputtering of Pt followed by etching in a warm aqueous solution of \textit{aqua regia} and obtained such films using this completely CMOS compatible process.

(iii) Using the X-ray photoelectron spectroscopy we have verified the structure and composition of the formed $\text{Pt}_3\text{Si}/\text{Pt}_2\text{Si}$ films; we have estimated the thickness of the $\text{Pt}_3\text{Si}$ layer of the films and found it to be equal to $\sim 2.6$ nm; the thickness of the $\text{Pt}_3\text{Si}/\text{Pt}_2\text{Si}$ films has been found to be $\sim 8.2$ nm. The obtained estimates practically coincide with those made on the basis of our previous data of the X-ray phase analysis [6].

(iv) We assume that the $\text{Pt}_3\text{Si}$ layer is formed from the $\text{Pt}_{95}\text{Si}_{15}$ layer, which appears under a Pt film during magnetron sputtering [6], as a result of Pt removal by wet etching.

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