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Electronic structure and spatial architecture of chemically deposited high-phosphorus nickel coatings for application in advanced microelectronics technologies

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Abstract

Objectives: This article examines the suitability of chemically deposited high-phosphorus nickel-phosphorus coatings as barrier layers for Through-Silicon Via (TSV) technology. Energy-dispersive X-ray microanalysis revealed that the phosphorus content in the coating is 10.2 wt. % (17.8 at. %). This high phosphorus concentration ensures the coating remains in an amorphous state, which is a critical prerequisite for effective barrier performance.

Experimental: Using X-ray photoelectron spectroscopy and soft X-ray spectroscopy, it was determined that the spherical globular formations comprising the coating have a core–shell structure. It was also demonstrated that the phosphorus concentration in the shell is higher than in the core.

Conclusions: The results obtained are of significant interest for advancing modern semiconductor manufacturing technologies, particularly in the area of heterogeneous 3D integration.

Keywords: Electroless nickel plating, High-phosphorus nickel coatings, Barrier layer, TSV technology, Heterogeneous 3D integration

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1. Introduction

Heterogeneous 3D integration technology is widely regarded as the most promising approach for advancing silicon microelectronics. The primary advantages of this technology include a significant increase in electronic device performance, a simultaneous reduction in heat generation, and a substantial decrease in chip footprint on printed circuit boards [1, 2].

The manufacturing of microelectronic devices using 3D technology involves the formation of through-silicon via (TSV) interconnects within a silicon wafer. Typically, TSVs are filled with copper through electroplating, which requires the deposition of adhesion, barrier, and seed layers onto their sidewalls [3–7].

The uniformity and continuity of the barrier and seed layers significantly affect not only the quality of copper filling in TSV holes but also the performance characteristics of the finished semiconductor devices. Traditionally, barrier and seed layers are deposited by physical vapor deposition (PVD) [8]. However, as the aspect ratio (AR > 5) of TSV holes increases, obtaining conformal coatings becomes challenging [9]. An alternative approach for depositing a continuous barrier/seed layer is the chemical deposition of metals, particularly nickel [10–12]. In addition to the continuity of the barrier layer, a critical quality criterion is the amorphous nature of the resulting coating [13]. Chemically deposited nickel coatings with medium to high phosphorus content satisfy these requirements [14, 15], making them highly promising for application in advanced heterogeneous 3D integration technology.

In this study, high-phosphorus nickel coatings were deposited onto silicon substrates via electroless plating. We evaluated the spatial structure of the spherical grains comprising the nickel coating using techniques sensitive to variations in the electronic structure at different analysis depths.

2. Materials and methods

Electroless nickel coatings were deposited on a pre-oxidized, (100)-oriented monocrystalline silicon substrate.

The electroless nickel plating bath composition consisted of 0.08 mol/L nickel chloride ($NiCl_2 \cdot 6H_2O$), 0.28 mol/L sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) as the reducing agent, 0.2 mol/L aminoacetic acid (NH_2CH_2COOH) as the complexing agent, and 0.12 mol/L sodium acetate (CH_3COONa) as the buffering additive. The solution pH was maintained at 5.5 by adding a 10% aqueous NaOH solution. The electroless nickel coating was deposited for 3 minutes at 80 °C.

The surface morphology and elemental composition of the obtained coating were analyzed using a Quattro-S scanning electron microscope equipped with an EDAX Octane Elect Plus EDS system for energy-dispersive X-ray microanalysis. X-ray photoelectron spectra (XPS) of Ni 2p and P 2p were acquired using a SPECS spectrometer (Germany). The spectra were excited by Mg Kα radiation (E = 1253.6 eV). Surface profiling of the samples was performed by sputtering with argon ions (Ar+) at an energy of 3 keV and an ion current density of 10 μA/cm^2 for 2 minutes. X-ray emission P $L_{2,3}$ spectra were obtained using an RSM-500 X-ray spectrometer monochromator at various analysis depths ranging from 10 to 120 nm.

3. Results and discussion

Fig. 1a presents a micrograph of the surface of the nickel coating deposited on a silicon substrate. Scanning electron microscopy (SEM) reveals globular, spherical formations on the coating surface. The most common globule size is approximately 200 nm; however, larger formations measuring 400–500 nm are also observed. Energy-dispersive X-ray spectroscopy (EDX) analysis indicates that the phosphorus content in the coating is C_P = 10.2 wt. % (17.8 at. %), classifying it as a high-phosphorus coating.

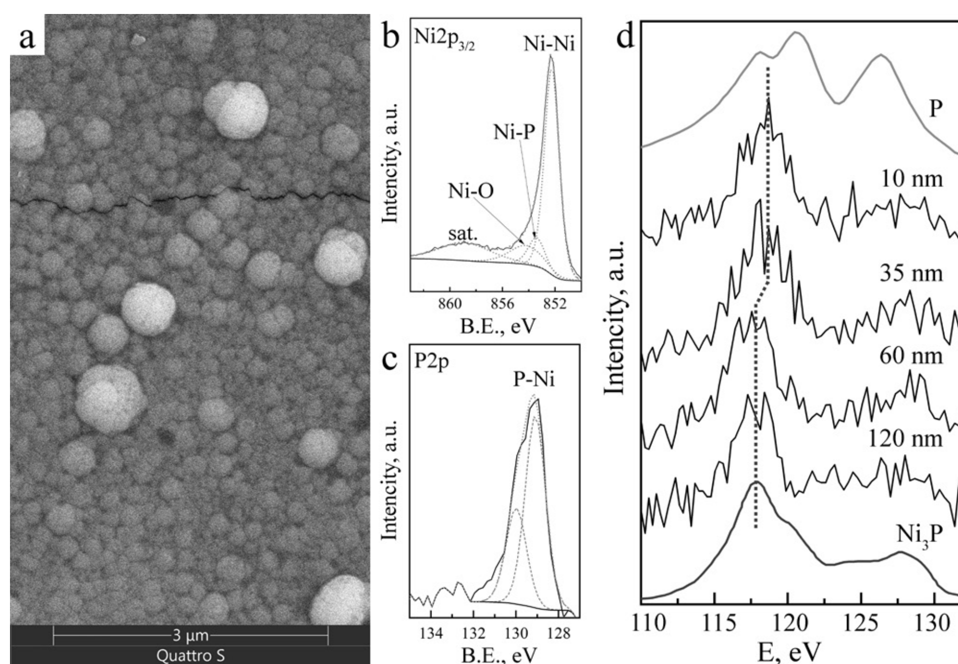

Fig. 1. Results of studies of chemically deposited nickel coating using the following methods: a – scanning electron microscopy, b, c – X-ray photoelectron spectroscopy and d – ultra-soft X-ray emission spectroscopy

X-ray photoelectron spectra of nickel ($Ni2p_{3/2}$) and phosphorus (P 2p) are presented in Figs. 1b and 1c, respectively. According to the XPS data (Fig. 1b), nickel in the coating exists in metallic (Ni–Ni, 852.2 eV) [16, 17], oxide (Ni–O, 854.2 eV) [18], and phosphide (Ni–P, 853.1 eV) [19] states. The P 2p spectrum (Fig. 1c) exhibits a single peak at 129.1 eV ($2p_{3/2}$), corresponding to the formation of nickel phosphide. Thus, the XPS data indicate that all phosphorus in the coating is bonded to nickel. Using the relative sensitivity factor method [20], the phosphorus concentration in the surface layers of the coating was calculated to be C_P = 23.2 at. %. This phosphorus concentration, determined from XPS spectral analysis, exceeds the previously reported value obtained by EDX (17.8 at. %), suggesting a non-uniform distribution of phosphorus atoms between the surface and the bulk of the nickel globular formations.

Fig. 1d presents the results of a layer-by-layer analysis of the nickel coating using ultra-soft X-ray emission spectroscopy (USXES). According to the USXES data, all phosphorus in the coating is chemically bound to nickel. Furthermore, the experimental P $L_{2,3}$ spectra for phosphorus at analysis depths of 120 nm and 60 nm closely match the shape of the reference spectrum for the Ni_3P phase. At shallower depths of 10 nm and 35 nm, a shift of the main spectral maximum toward higher energies is observed. This shift is attributed to an increased concentration of phosphorus in the surface layers of the coating globules.

Fig. 2 presents a schematic representation of the structure of the spherical nickel-coated globules. Based on the average size of the globules (approximately 200 nm) and the results of the

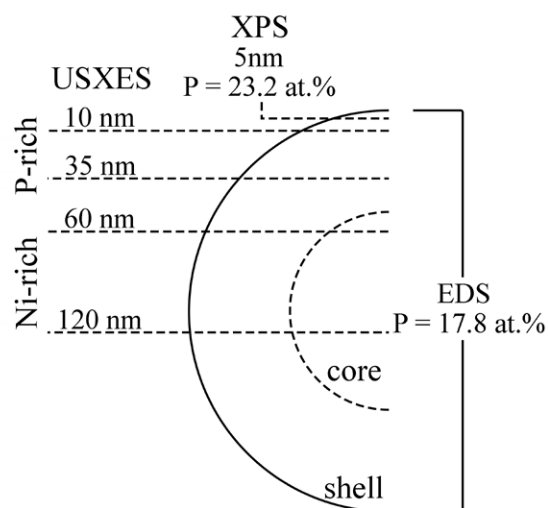

Fig. 2. Schematic representation of nickel coating globules

layer-by-layer spectral analysis of the nickel coating, it is evident that the surface layers of the nickel globules are enriched with phosphorus atoms. The phosphorus content decreases with increasing analysis depth. Therefore, the structure of the globular formations comprising the nickel coating can be described using a core-shell model, in which the core is enriched with nickel atoms and the shell is enriched with phosphorus atoms.

4. Conclusion

This study demonstrates the potential of electrolessly deposited nickel coatings as barrier layers in through-silicon via (TSV) technology. The phosphorus content in the nickel coating deposited on an oxidized silicon substrate is C_P = 10.2 wt. % (17.8 at. %), classifying it as a high-phosphorus coating.

Using X-ray photoelectron spectroscopy and ultra-soft X-ray emission spectroscopy, both capable of layer-by-layer analysis up to a depth of 120 nm, it was demonstrated that the spherical globular formations comprising the nickel coating can be described by a core-shell model. In this model, the shell contains a higher concentration of phosphorus atoms than the core.

The results obtained are significant for establishing a scientific and technical foundation in advanced semiconductor manufacturing technologies, particularly in the field of heterogeneous 3D integration.

Author contributions

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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