Influence of alloying elements on the phase formation of ultrathin Ni (<10nm) on Si(001) substrates

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ABSTRACT

The influence of Ni thickness on the formation of Nickel silicides was systematically investigated between 0 and 15nm. Annealing thickness gradients distinguishes films that agglomerate (>5nm) and films that are morphologically stable (<5nm). Alloying the initial Ni layer influences this critical thickness to higher (Al, Co) and lower (Ge, Pd, Pt) values. Pole figures and in situ XRD provides information to understand this observed shift in critical thickness.

INTRODUCTION

Over the past decades, nickel mono-silicide NiSi has become one of the preferred materials to enhance contacting in modern silicon-based semiconductor devices. However, the formation of a useable NiSi contacting layer is challenged by the continued miniaturization in the micro-electronics industry. As the silicide thickness is reduced, it is more likely to agglomerate which results in a severe increase of the sheet resistance. Therefore it is crucial to stabilize the morphology of thin silicide films, either by altering the microstructure of the NiSi phase or by exploring the use of alternative phases that are more resistant to agglomeration.

De Keyser *et al.* [1] recently reported that below a critical thickness ($t_{critical}$) of 5 nm, ultrathin Ni films result in surprisingly stable silicide layers. A Ni film that is slightly thicker than $t_{critical}$ (e.g. 6 nm) forms a NiSi silicide that starts to degrade around 600°C. In contrast, a slightly thinner Ni film (e.g. 4 nm) forms a continuous silicide that remains stable up to 850°C.

EXPERIMENTAL AND RESULTS

Deposition and examination through thickness gradients

To investigate this peculiar behavior, we used a home-built combinatorial sputter system in order to deposit a Ni gradient. In one single deposition, a film was deposited on a 6 inch Si (001) substrate with an increasing Ni thickness from 1 nm on one end of the wafer, to 15 nm on the other end of the wafer. This gradient was then used as a "thickness library" to systematically investigate the solid state reaction between Ni and Si, where the Ni thickness is fixed by the position on the wafer (Fig. 1a). As we will use further below, this film could optionally be alloyed with a constant concentration of a secondary element.

The effectiveness of using thickness gradients in studying agglomeration is illustrated by the visual determination of $t_{critical}$ in a single deposition. After annealing a Ni gradient to 700°C, a dark and light region appeared on the substrate with a clear transition border. (Fig. 1b) SEM confirmed that the dark region coincides with an agglomerated silicide layer, whereas the lighter part of the wafer showed a stable morphology. The border between these two regions, visible in the middle SEM image of Fig. 1b, determined the value of $t_{critical}$ at 4.8 nm. The stability of the silicides was confirmed by sheet resistance measurements during heating (Fig. 1c) for temperatures up to 850°C. We can therefore conclude that the gradient method is in agreement with literature.

Influence of alloying

A second series of samples were prepared to investigate the influence of alloying elements on the critical thickness. It is broadly reported that adding a secondary element to the initial Ni layer can severely influence the phase formation and stability for thicker silicides [2, 3, 4]. We have deposited thickness gradients of Ni alloyed with 10 at.% of six different elements (Al, Si, Co, Pd, Ge and Pt) and determined the critical thickness using the previously discussed method (Fig. 2). We observe that the value for $t_{critical}$ is larger when alloying with Al and Co, and lower when Ge, Pd and Pt is added to the Ni layer.

The observed variation of the critical thickness was further investigated by focusing on the crystalline phase of the formed silicide. As we will briefly discuss in the following, the ultrathin film regime is distinguishable from thicker films by the absence of the NiSi phase. *In situ* XRD experiments where performed at the X20C beamline of the *National Synchrotron Light Source* (NSLS) located in Brookhaven, NY, USA. Films with a thickness above $t_{critical}$ follow the known formation path where the as-deposited Ni layer reacts with the Si substrate, first forming a metal-rich silicide, eventually followed by the formation of NiSi (Fig. 3a and b). The *in situ* XRD measurements for samples in

the ultrathin film regime (Fig. 3c) lack the necessary peaks for a clear understanding of the phase formation. This suggests that the formed silicide grows with a strong epitaxial texture, making it invisible for the *in situ* XRD measurements using a Bragg-Brentano-based setup. Pole figures overcome this limitation and where measured on 25 different samples quenched at 700°C at the X20A beamline of the NSLS. The use of a linear detector results in a series of 640 pole figures covering the d-spacing between 1.54 and 4.43Å, allowing unambiguous phase identification (Fig. 4). For films above the critical thickness, we could clearly identify the NiSi phase with an axiotaxy-type texture [5]. Samples below the critical thickness lacked any diffraction from this phase and only displayed epitaxial dots. The only silicide that can be present in these films is $NiSi_2$ with an epitaxial orientation exactly matching the Si substrate.

The absence of NiSi in the ultrathin films helps us to understand the observed shift in the critical thickness when the Ni layer is alloyed. Indeed, from ternary phase diagrams we know that Pt, Pd and Ge are soluble in NiSi and insoluble in $NiSi_2$, consequently hindering the formation of the latter. In contrast, Al and Co are known to be soluble in $NiSi_2$ and not in NiSi. As such, Al and Co promote the formation of an epitaxial $NiSi_2$ phase, whereas Pt, Pd and Ge promote the formation of the agglomerating NiSi phase

CONCLUSIONS

The formation of agglomerating NiSi does not occur when annealing Ni films with an as-deposited thickness of 5 nm.
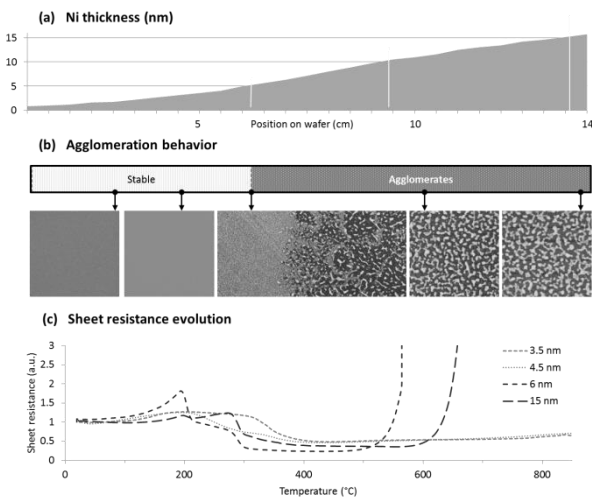
Instead, the formed $NiSi_2$ silicide remains morphological stable and grows epitaxially on the Si(001) substrates. Thickness gradients allow systematic investigation of this critical behavior. We have observed that the value of this critical thickness can be influenced by alloying. Mixing Al or Co with the initial Ni film promote the formation of $NiSi_2$ and consequently shift the critical thickness to higher values whereas Ge, Pd or Pt result in a lower critical thickness. This can be understood on the basis of solubility arguments.

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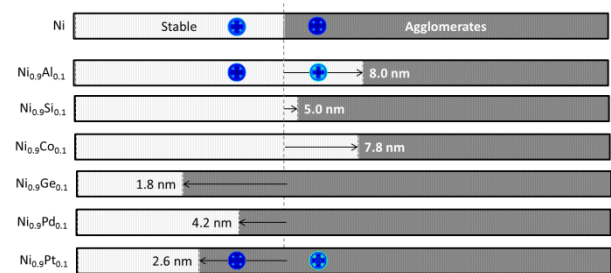
Fig. 1 1: The value of the critical thickness was determined by annealing a Ni thickness library. **(a)** The thickness of the Ni layer was fixed by its position on the wafer and **(b)** annealing to 700°C reveals that films thinner than 4.8 nm do not agglomerate. **(c)** From sheet resistance measurements during heating it can be concluded that the morphology of these films remains stable up to 850°C.

Fig. 2: The evaluation of the critical thickness t*critical* when the as-deposited Ni layer is alloyed with 10 at. % of a secondary element (Al, Si, Co, Ge, Pd and Pt). The blue circles indicate the positions of the samples which are displayed in Figure 4 and will be discussed later.
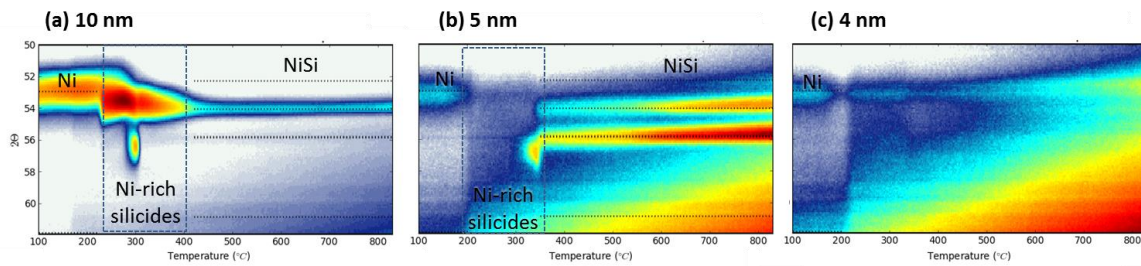
Fig. 3: *In situ* XRD during heating for different thicknesses ($\lambda = 1.54$ Å) of pure Ni on Si(001). **(a, b)** Layers above $t_{critical}$ reveal the expected formation of Ni -> Ni-rich silicides -> NiSi. **(c)** Thinner films do not provide a clear diffraction pattern.
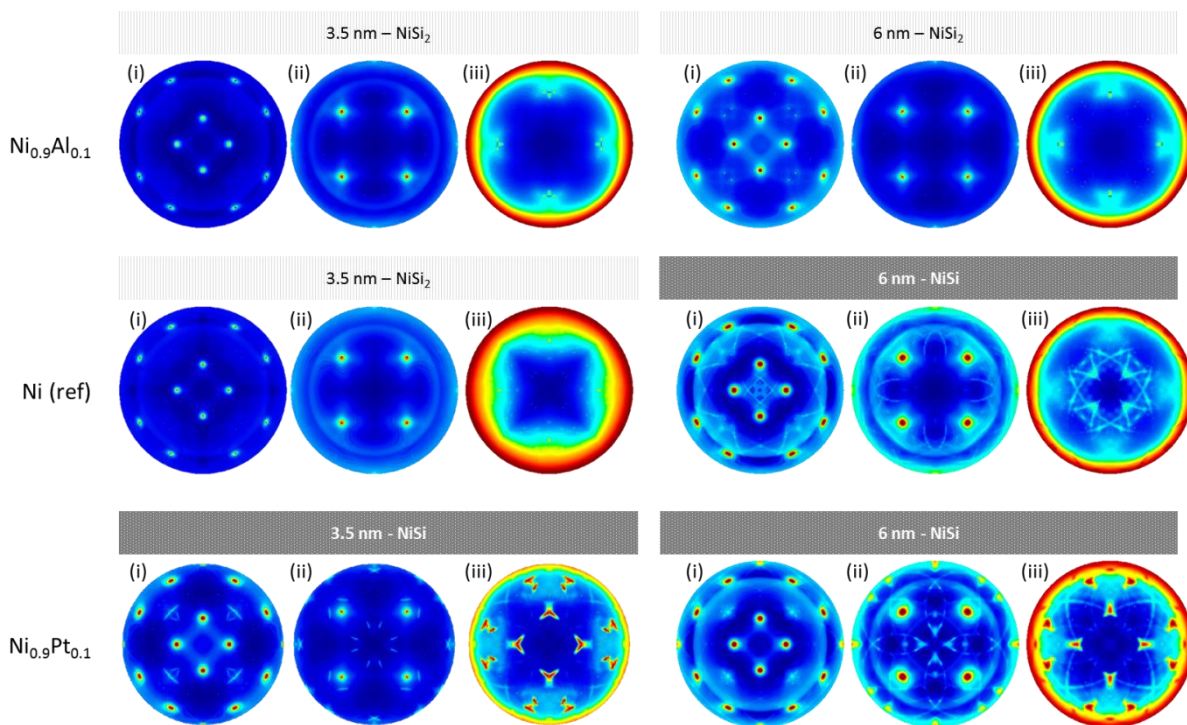

Fig. 4: A selection of the measured polefigures illustrates the influence of both thickness and alloying on the phase formation. Three pole figures are displayed for each sample for three different d-spacings: (i) 1.64Å, (ii) 1.91Å and (iii) 2.86Å. The pole figures which only display spots of high intensity (corresponding to poles of the Si substrate and of epitaxial $NiSi_2$) coincide with non-agglomerating samples. The other pole figures show features with a round shape, corresponding with axiotaxy-textured NiSi [5].