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Lamellar-structured Ni-silicide film formed by eutectic solidification

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ABSTRACT

Pt-doped NiSi–$NiSi_2$ thin films in a uniform lamellar structure with a periodicity on the scale of a few tens of nanometers were formed on Si(001) substrates using a continuous laser scanning process. When the Pt-doped NiSi film was melted at high temperatures and was supercooled at high solidification rates (a high scanning speed of over 200 mm/s), a NiSi–$NiSi_2$ lamellar structure evolved while interacting with the underlying Si substrate and following the classical eutectic solidification path. The lamellar spacing could be easily controlled by the laser scanning speed. In addition, the periodically formed, nearly single-crystalline NiSi and $NiSi_2$ phases exhibited epitaxial relationships with each other and also with the Si(001) substrate. It is believed that this novel NiSi–$NiSi_2$ lamellar structure can be used as a template for application areas requiring an electrode with a line/space pattern on the scale of a few tens of nanometers that can be prepared without using costly photolithographic processes.

1. Introduction

Once a certain material in a bulk or a thin-film form is melted and quenched, various interesting phases and physical properties can evolve, depending on the material's composition and solidification rate. In particular, eutectic alloys in bulk form have been extensively studied in many academic and industrial fields for their spontaneous phase separation from liquid to form various unique structures including a lamellar structure under constitutional supercooling conditions [1,2]. However, the similar phase separation phenomena of eutectic thin films under melting and rapid solidification have not yet been widely studied [3–7]. Particularly for metal-silicide films, only a few papers have reported on the lamellar structure formation of a Co-silicide system on a SiO_2 film using a laser annealing process [5–7].

In the 1980s, the laser annealing process was largely applied to the formation of various transition metal silicide films to study the phase transition kinetics, and also to induce the appearance of highly metastable phases [8]. Laser annealing is an ideal method to study the melting and re-solidification phenomenon under the constitutional supercooling condition of thin films owing to its localized surface heating at high temperatures. Furthermore, the re-solidification process in steady- and non-steady-state conditions can be easily controlled by adjusting the laser exposure time or the scanning speed. Recently, we applied this melting/quenching method to a Pt-doped Ni-silicide system using continuous laser annealing (at a scanning speed of approximately 75 mm/s) and obtained a thermally robust (up to 800 °C), chemically homogeneous, and lowly resistive $Ni_{1-x}Pt_xSi$ film on a Si substrate [9]. Here, Pt was incorporated into the Ni-silicide film to enhance its thermal stability [9–11].

Herein, we used a much higher laser scanning speed (over 200 mm/s) for the melting/quenching process of the $Ni_{1-x}Pt_xSi$ film and observed an interesting eutectic phase separation: namely, a lamellar structure was formed directly on the Si(001) substrate and

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consisted of Ni-monosilicide (NiSi) and Ni-disilicide ($NiSi_2$) phases. The formed lamellar structure was uniform, with a controllable periodicity on the scale of several tens of nanometers and could prove useful in many device applications that require large-area electrode formation without using a highly expensive nano-patterning process. The detailed microstructural characteristics of the unique lamellar structure were investigated, and their formation mechanism was elucidated.

2. Experimental details

To form Pt-doped Ni-silicide eutectic thin films, we sputter-deposited approximately 18 nm-thick $Ni_{1-x}Pt_x$ films (nominally, $x \sim 0.1$) capped with 10 nm-thick TiN on n^+ Si wafers immediately after hydrogen fluoride (HF) cleaning. The first silicidation to form a preliminary Ni_2Si phase was performed using rapid thermal annealing (RTA) at 260 °C for 30 s, and then the unreacted metal (including the TiN capping layer) was wet-stripped. For the melting/quenching process of the preliminary Ni_2Si phase at different supercooling rates, samples were exposed to a continuous diode laser beam with an 810 nm wavelength at various scanning speeds (214, 250, and 300 mm/s) and at different local surface temperatures ranging from 950 °C to 1200 °C, whereas the substrate susceptor was heated at ~430 °C to transform Ni_2Si into NiSi and to minimize the thermal gradient, which can induce wafer breakage due to thermal shock [9]. Additional sample preparation procedure can be found in our previous report [9].

The sheet resistance (R_s) and surface morphology of the formed films were measured using a micro four-point probe system and a scanning electron microscope (AMAT, SEMVision™ G7), respectively. The detailed microstructure of the films was examined using a transmission electron microscope (FEI, Titan^3™ 80–300) operating at an electron acceleration voltage of 300 kV and having image and probe spherical aberration correction functions. For the transmission electron microscopy (TEM) observation, several TEM specimens with thicknesses of approximately 50 nm were prepared along three orthogonal directions using a focused ion beam tool (FEI, Helios 460F1). Selected-area electron diffraction patterns (SADPs) were acquired with a camera length of 285 nm and an aperture diameter of 40 nm. To obtain the accurate atomic composition of the films, we analyzed the samples using an atomic probe tomography (APT) microscope (AMETEK, LEAP 5000XS) with a flight distance of 200 nm and a 355 nm-wavelength UV laser operating at 12 pJ of pulse energy and 250 kHz of pulse rate.

3. Results and discussion

3.1. Formation of the eutectic lamellar structure

Fig. 1 shows the change in the measured R_s of the films as a function of the laser annealing temperature at different scanning speeds (214, 250, and 300 mm/s). All the samples underwent conduction heating (substrate heating in the laser system at ~430 °C for 70 s) during laser scanning. For comparison purposes, the R_s value of the reference sample that underwent identical conduction heating only is also included in the graph. The measured R_s of the reference film corresponded to a resistivity of approximately 30.8 μΩ cm when considering the formed film thickness of 22.4 nm (Fig. S1 in the Supplementary Information), which indirectly verified the formation of a Ni-monosilicide phase ($Ni_{1-x}Pt_xSi$) before/during laser annealing [12,13]. In the case of the samples that underwent laser annealing at sub-melting temperatures ($T \lesssim 1050$ °C [9,13]), the measured R_s values were slightly lower than that of the reference sample, which indicated that the formed film was still a $Ni_{1-x}Pt_xSi$ film. However, when the laser

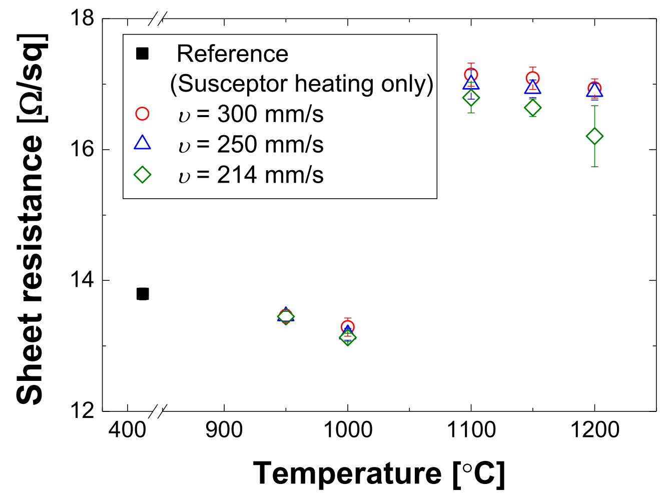

Fig. 1. Sheet resistance of the Ni-silicide films as a function of the laser annealing temperature at different scanning speeds. All the samples including the reference sample underwent simultaneous heating on the susceptor at ~430 °C for 70 s.

annealing temperature was above the melting condition, a R_s increase of approximately 23% compared to the reference sample was observed for all the samples at different scanning speeds. Morphological agglomeration and phase transition to a highly resistive $NiSi_2$ phase generally resulted in an abrupt R_s increase with increasing annealing temperature [14,15]. Because the annealing temperature increase resulted in a slightly decreasing trend in R_s, we could exclude the agglomeration phenomenon and therefore suspected that the films that formed above the melting temperatures were a mixture of lowly- (monosilicide) and highly resistive (disilicide) phases. There could also be a possible thickness thinning effect by slight sublimation of the preformed Ni-silicide during high-temperature laser annealing [16].

To understand the observed R_s behavior for different laser annealing temperatures, we collected plan-view scanning electron microscopy (SEM) images for the samples laser-scanned at the highest speed of 300 mm/s, as shown in Fig. 2; other samples scanned at lower speeds (214 and 250 mm/s) showed similar morphological trends at all temperature ranges of the experiment (Fig. S2 in the Supplementary Information). For the reference sample (see Fig. 2a), a continuous and poly-crystalline microstructure with a grain size of approximately 400 nm was observed, which supported the formation of a mono-silicide phase without agglomeration. Here, the grain size was roughly estimated by counting the dark lines representing the grain boundaries across an arbitrary line on the SEM image. Similar morphological characteristics to those of the reference sample were observed on the samples that were laser-scanned under a sub-melting condition at 950 °C and 1000 °C, as shown in Fig. 2b and c, respectively. The slightly gradual decrease in R_s with a temperature increase shown in Fig. 1 can be understood by considering a possible grain growth; the estimated grain sizes of the samples annealed at 950 °C and 1000 °C were approximately 400 and 440 nm, respectively. On the contrary, the samples laser-scanned above a melting condition (1100–1200 °C) revealed the formation of a periodic lamellar structure with alternating dark and bright contrasts, as shown in Fig. 2d–f, which suggests that the observed R_s increase was mainly due to the phase separation during the melting/quenching processes at a high laser scanning speed (i.e., high solidification rate). Here, the boundaries between the alternating dark and bright regions were parallel to the laser-scanning direction. It should be noted that this formation of a lamellar structure contrasts with that