FORMATION OF Si-ENRICHED METASTABLE COMPOUNDS IN THE Pt–Si SYSTEM USING ION BOMBARDMENT AND POST ANNEALING

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Silicon-enriched Pt–Si mixed layers have been formed by implanting through a thin PtSi film on a Si substrate. Subsequent thermal annealing at 400–500°C resulted in the formation of well-defined phases. The compounds have compositions close to Pt_2Si_3 and Pt_4Si_9 and possess properties of metastable phases.

In the realm of classical metallurgy, investigations are directed primarily toward systems produced under equilibrium conditions. Metastable alloys, which cannot exist in thermal equilibrium, have been prepared by use of quenching techniques such as splat cooling [1] and vapor quenching methods [2], as well as by ion-implantation technology [3]. Substitutional solid solutions with compositions in excess of the equilibrium concentration have been achieved [4].

Metastable films produced by ion implantation into metal are of considerable interest due to the possibility of creating alloys with unique physical properties [3]. Substantial modifications of surface properties of the materials in fields such as corrosion, adhesion, wear and hardness have been observed. However, the major drawback to high-dose implantation, from the technical point of view, is that ion doses greater than 10^{17} ions/cm^2 are required in order to produce concentrations of implanted ions in excess of a few atomic percent. Aside from the long implantation time, the process is limited by sputtering effects which establish the maximum concentration that can be achieved by implantation [5].

The present work relies on the concept that primary ions have the ability to produce enhanced atomic migration within the ion track such that significant "atomic mixing" can be initiated between a surface layer and the substrate during ion bombardment [6]. For instance, with a thin Pt layer on top of a Si substrate, we have observed that Pt-silicide could be formed near the Pt–Si interface under rather low-dose ($\approx 10^{15}$ cm^{-2}) ion bombardment [6]. Implantation with higher ion doses will then result in the formation of a Si-enriched Pt–Si mixed layer. This Si-enriched composition cannot be achieved by normal thermal treatment, where the PtSi phase is the most Si-enriched compound [7]. The purpose of this work was to investigate the effect of post annealing on the composition and structures of the Si-enriched mixed layers.

Thin Pt films a few hundred Å thick were prepared by electron-beam evaporation of Pt onto ⟨100⟩ oriented single-crystal Si substrates. PtSi layers were then formed by heating the samples at 350°C for 15 min in a vacuum furnace with pressure less than 1×10^{-6} Torr. The samples were implanted at room temperature with 200–300 keV Xe^+ beams to doses ranging between 5×10^{14} cm^{-2} and 1×10^{16} cm^{-2}. Isothermal annealing was performed in a vacuum furnace at temperatures up to 800°C.

Rutherford backscattering analysis (RBS) with 2.0 MeV $^4He^+$ beam was used to measure the composition profiles. Glancing angle X-ray analysis with Cu Kα radiation in a Read camera and Seemann–Bohlin diffraction configuration [8] were also employed to examine the phase structures of the surface layer.

Fig. 1a shows the backscattering spectra of a sample (labeled as A) with a 350 Å PtSi film on a Si substrate bombarded with 300 keV Xe ions to a dose of 1×10^{15} cm^{-2}. The data (dashed curve) indicate that the Pt–Si layer becomes Si-enriched due to the mixing

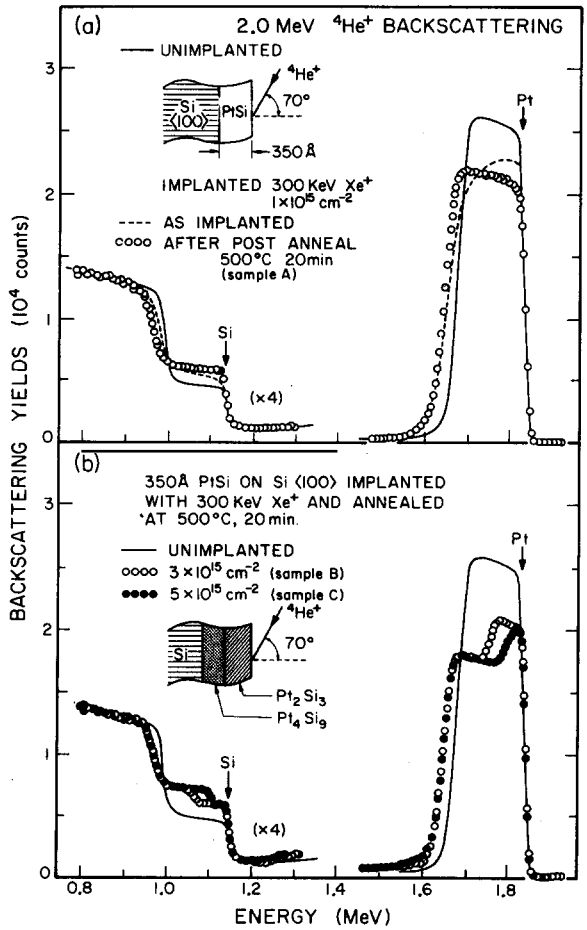

Fig. 1. Backscattering spectra which show the formation of Si-enriched Pt–Si compounds. The samples were originally a 350 Å PtSi film on a Si substrate and bombarded with 300 keV Xe^+ to various doses. (a) For Xe^+ dose of 1×10^{15} cm^{-2}, post annealing at 500°C for 20 min results in the formation of compound with composition close to Pt_2Si_3. (b) For higher Xe^+ dose, the Pt–Si layer is separated into two distinctive regions with a second phase (Pt_4Si_9) formed beneath the surface layer (compound Pt_2Si_3).

effect. The composition of layers varies in depth with the Si/Pt concentration ratio varying from 1.34 at the surface to 1.75 at the interface. In addition, glancing angle X-ray analysis showed the disappearance of diffraction patterns of the PtSi phase. However, post anneal at 500°C for 20 min substantially modified the structures of the surface mixture. First, the composition was uniform over the layer thickness with a Si to Pt concentration ratio close to 1.5 ± 0.04. This ratio has been found in several samples with slightly different film thicknesses and Xe ion doses, and was quite reproducible within experimental errors. Secondly, X-ray analysis showed the presence of crystalline diffraction lines in contrast to the structureless pattern observed after bombardment and before heat treatments. Fig. 2a shows the Read camera diffraction pattern for sample A. This pattern (labeled as A) has been compared with that of PtSi, Pt_2Si and poly-Si and the line positions are shown in fig. 2c. The diffraction lines of sample A cannot be matched with those of pure phases or mixtures of PtSi, Pt_2Si and poly-Si. We have not yet identified the crystal structure of the compounds and labeled them according to the composition determined by RBS.

Implantation with higher doses (from 2×10^{15} cm^{-2} to 1×10^{16} cm^{-2}) have also been carried out.

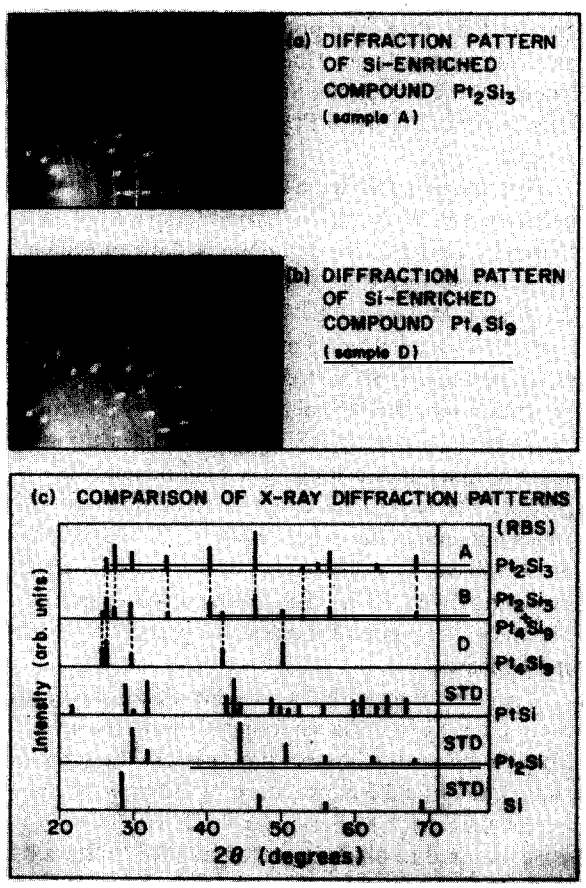

Fig. 2. X-ray diffraction patterns (taken from Read camera) for (a) compound Pt_2Si_3, and (b) compound Pt_4Si_9, (c) comparison of the diffraction patterns with that of standard PtSi, Pt_2Si and polycrystalline Si (denoted as STD).

Fig. 1b shows the backscattering spectra of two samples (B and C) implanted with different doses, but with the same annealing conditions. The surface layer is separated into two distinctive regions as indicated by the step in the Pt and Si signals. The layer on the surface has composition close to Pt_2Si_3, but the layer underneath is even more Si-enriched with a composition near Pt_4Si_9. The interface between these layers is well defined and shifts progressively toward the surface with increasing ion doses. Finally, a uniform layer with composition near Pt_4Si_9 was established for Xe^+ doses greater than 6×10^{15} cm^{-2} (up to 1×10^{16} cm^{-2}). X-ray analysis of the sample with a Pt_4Si_9 composition (labeled as D) showed the presence of crystalline diffraction pattern with a slightly diffused configuration (fig. 2b). The diffraction lines do not fully agree with those belonging to Pt_2Si_3 composition, or PtSi, Pt_2Si and poly-Si (fig. 2c). Other samples with double layer structures have also been analyzed. All the diffraction lines can be identified to belong to either Pt_2Si_3 or Pt_4Si_9 composition as indicated in fig. 2c.

Post annealing between 200°C and 800°C has been performed to study the formation temperature and thermal stability of the compounds. No appreciable reaction was observed for annealing at or below 300°C for 1 hour. Between 400°C and 500°C the compounds could be formed after 15 min annealing. Slightly higher temperature (550°C) treatment resulted in the transformation into the PtSi phase. X-ray analyses showed the presence of strong PtSi diffraction lines along with some residual lines belonging to Si-enriched compounds. The latter lines disappeared completely for annealing temperatures above 600°C. Similar transformations have been observed at 500°C for prolonged annealing time ($\geq$ 1 h). The results suggest that the Si-enriched compounds possess the properties of metastable phases.

The formation of the metastable phases does not require inert gases. The experiments were repeated using Si ions as the bombarding species. The same results were obtained as produced by Xe bombardment except that much higher doses ($\geq 2 \times 10^{16}$ cm^{-2}) were required to obtain equal amount of "intermixing". The difference in dose is because Xe is much heavier than Si and, hence, more effective in initiating atomic mixing [6].

The consequence of ion-induced intermixing is to redistribute Pt into the deeper region of the sample such that the layer becomes enriched in Si. This Pt–Si intermixed layer is structureless (presumably amorphous) due to the bombardment damage and the composition varies with depth (more Si-enriched in the deeper region as shown in fig. 1a). If thermal annealing can provide a driving force for compound formation, the nucleation process is likely to occur near the region where the composition is close to the stoichiometry of a particular compound. Consequently, the presence of two phases (fig. 1b) is possible due to the variation of the composition over the layer thickness. On the other hand, nucleation of the second phase (Pt_4Si_9) will be favored with increasing ion dose since the layer becomes progressively more Si-enriched due to the mixing effect. This argument seems consistent with the observed results as shown in fig. 1b.

In summary, by using ion bombardment, we have been able to produce intermixed layers as a result of ion-induced atomic mixing between a deposited layer and a substrate. Metastable alloys with unusual compositions could be formed after post thermal annealing. This opens the possibility of making thin film materials with compositions and structures unachievable by traditional metallurgical means. On the other hand, the results also suggest that this highly "efficient" ion-induced atomic mixing process may be an alternative approach for ion-beam material modification, but as dose levels one or two orders of magnitude lower than those used in high-dose implantation.

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