Kinetics and moving species during Co_2Si formation by rapid thermal annealing

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We have investigated the growth kinetics and identified the moving species during Co_2Si formation by rapid thermal annealing (RTA). For the kinetics study, samples which consisted of a thin Co film on an evaporated Si substrate were used. To study which species moves, samples imbedded with two very thin Ta markers were employed. Upon RTA, only one silicide phase, Co_2Si, was observed to grow before all Co was consumed. The square root of time dependence and the activation energy of about 2.1 ± 0.2 eV were observed during the Co_2Si formation up to 680 °C. The marker study indicated that Co is the dominant mobile species during Co_2Si formation by RTA. We conclude that Co_2Si grows by the same mechanisms during RTA and conventional thermal annealing.

I. INTRODUCTION

In semiconductor device technology, rapid thermal annealing (RTA) has appeared as an effective solution to several problems associated with the conventional thermal annealing process. As the device dimensions are reduced, shallow junctions, high-doping levels, and reduced defect density are required. While it is difficult to achieve these goals with conventional furnace annealing, it has been reported that in RTA, at a higher temperature and shorter time of annealing, the diffusion of implanted dopants can be precisely controlled while activating the impurities and annealing the implantation damages.[1,2] RTA also has an advantage in uniform heat treatment of large diameter wafers, which is more difficult to achieve in a standard furnace due to edge heating and cooling.[3,4] With the above advantages, RTA has been used for silicide formation and extensive studies for device applications have been recently reported.[5] For example, Morgan *et al.*[6] have shown that self-aligned $CoSi_2$ contacts and interconnects can be successfully fabricated using RTA process.

The essential knowledge in understanding silicide formation should include that of the moving atomic species, transport mechanisms, and formation kinetics. No identification of the moving species during silicide formation by RTA has been reported. In several systems, such as Ti,[7,8] Pd,[9,10] Pt,[11] and Er,[12] the silicide formation kinetics during RTA have been investigated. Although it may be intuitively expected that RTA should not bring anything significantly new compared with conventional annealing, research is still desirable to clarify the process.

As an example, it has been reported that for PtSi, the thickness linearly increases with annealing time t [11] in RTA, rather than with $t^{1/2}$ [13] as in furnace annealing. Furthermore, the results of marker experiments indicate that the moving species, and therefore the atomic transport mechanisms, do not always concur with each other when the processing method is changed. For example,[14] while Ni is the only moving species during Ni_2Si formation in thermal annealing at 250 °C, both Si and Ni move when Ni_2Si is formed by ion mixing at 110 °C. This result leads to the interesting hypothesis that the silicide formation temperature may affect the atomic transport mechanism and the moving species. Therefore, it is of interest to investigate this question at the elevated temperatures typical of RTA.

II. EXPERIMENTAL PROCEDURES

Commercially available boron-doped p-type ⟨100⟩Si wafers of resistivity 5–13 Ω cm were ultrasonically cleaned with trichloroethylene, acetone, and methanol, and then etched in a 20% HF solution. After rinsing in deionized water, they were loaded into an oil-free multihearth electron-beam evaporation system. The evaporations were carried out at base pressure lower than 1×10^{-7} Torr. For the kinetics study, about 2000-Å Si was evaporated, followed by about 1560-Å Co. For the marker study, the following sequence of layers was evaporated as illustrated in Fig. 1; 125-Å Si, 13-Å Ta, 2000-Å Si, 50-Å Co, 10-Å Ta, 50-Å Si, and 850-Å Co. This choice allows the easy separation of the backscattering signals of the marker and the Co. Two thin layers of Co and Si are evaporated adjacent to the marker to embed the latter within a homogeneous Co_2Si layer after the preannealing step. This precaution minimizes the possibility of an interfacial dragging of the marker during subsequent silicide growth.[15] The uniformity of the deposited layer thicknesses was checked on several samples taken from different parts of the wafer. The differences in thickness were undetectable by backscattering spectra, all the samples from the same wafer were thus treated as being identical.

RTAs of the samples were carried out in an AG Associates HeatPulse 410 RTA unit under an ultrapure Ar atmosphere (99.999%). RTA temperatures for the kinetics study

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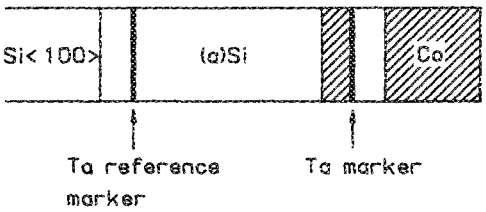

FIG. 1. Sample configuration used in the study of marker movement. The sequence of layers is: Si⟨100⟩ substrate, 125-Å Si, 13-Å Ta, 2000-Å Si, 50-Å Co, 10-Å Si, and 850-Å Co. The bottom layer of Ta is called "reference marker" to distinguish it from the marker.

ranged from 490 to 680 °C. For direct comparison between RTA and conventional furnace annealing, several samples were also annealed in a vacuum furnace. The vacuum during annealing was about 2×10^{-7} Torr and temperatures were 370, 400, and 450 °C. Preannealing was carried out for the marker samples; the conditions were 510 °C for 20 min in a vacuum of 2×10^{-7} Torr. The RTA temperatures for the marker study ranged from 615 to 685 °C. Compared with the typical furnace annealing temperatures used in kinetics studies[13] and marker experiments,[16] the present RTA temperatures are about 150 and 200 °C higher, respectively.

In both studies, after RTA processing, the ratios of Co and Si backscattering peak heights revealed a stoichiometry consistent with that of Co_2Si, the formation of which was also confirmed by x-ray diffraction. The Co_2Si thickness and the associated marker shifts in each case were measured by 2-MeV $^4He^+$ backscattering spectrometry. The marker shifts were determined relative to the reference Ta layer.

The accurate measurement of temperature is one of the most critical and difficult problems in RTA-related work. At present, the most widely employed method to measure temperature in RTA makes use of either an optical pyrometer or a thermocouple attached (or bonded) either to an actual sample or to a witness sample placed right next to the actual sample. However, it is reported[17] that, in either case, there are inherent limitations to the accuracy of the measurement.

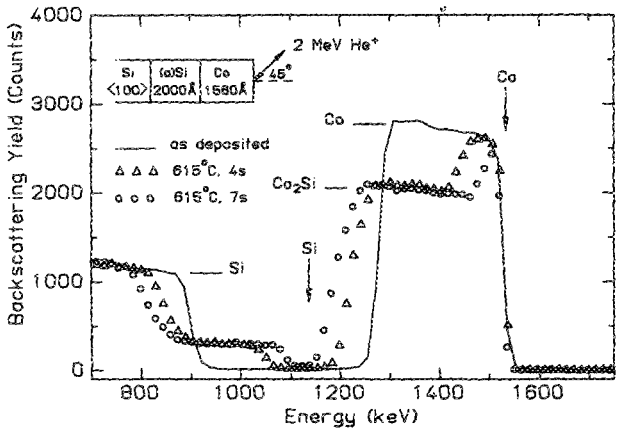

FIG. 2. 2-MeV $^4He^+$ backscattering spectra showing the progressive formation of Co_2Si at 615 °C. Spectra were obtained from the as-deposited sample (solid line), after RTA at 615 °C for 4 s (triangle) and 7 s (circle). The total scattering angle is 170°. The sample normal is tilted by 45° from the line of the incident beam in a plane perpendicular to that defined by the incident and the detected beams.

In this work, the accuracy of the temperature measurement was first checked by detecting morphological changes that indicated melting of a thin pure Al film deposited on an oxidized Si substrate of the size of our sample. A temperature reading short of 60–80 °C was given by the thermocouple of the sytem at the melting point of Al. This difference is believed to be the result of the inadequate thermal coupling of a bonding between the thermocouples and the Si wafer. To improve the accuracy of temperature measurements, we used the principle of resistivity change with temperature in Si. We made a delicate Si resistor composed of a small piece of Si similar in size and thickness to the samples used for the experiments, and two thin silver wires attached to it. When constant current passes through the Si piece, temperature can be determined by measuring the resistivity change. The thin silver wires allowed flexibility for the Si piece to be placed in the RTA chamber in exactly the same manner as an actual sample. This is necessary to exactly reproduce the thermal environment of actual samples.

Prior to its use for temperature measurement, the resistor was calibrated by measuring the change of resisitivity with temperature in a furnace. The accuracy of this calibration was $\pm$ 2 °C. Since the temperature fluctuation during the plateau of an RTA cycle was within $\pm$ 15 °C, the accuracy of the temperatures cited in this work is within $\pm$ 17 °C. The precision of this method of temperature measurement declines rapidly above about 700 °C.

III. RESULTS AND DISCUSSION

A. Kinetics

Figure 2 shows typical backscattering spectra indicating the progressive formation of Co_2Si during RTA. Spectra of as-deposited (solid line), after RTA at 615 °C for 4 s (triangle) and 7 s (circle), samples are presented with the calculated heights of Co, Si, and Co_2Si indicated with solid lines. The insert shows the configuration of an as-deposited sample.

Upon conventional thermal annealing, films of all transition metals on a Si substrate always form only one silicide at a time, barring impurity effects.[13] But contradictory results have been reported for Co. Some researchers[18,19] report that both Co_2Si and CoSi grow side by side upon the initial reaction of Co with Si. However, another paper[20] reports that only Co_2Si forms initially and that CoSi only appears once all the Co is consumed. In our work, both RTA and furnace annealing results agreed with the latter observation. As can be seen in Fig. 2, only one phase, Co_2Si, was visible in the backscattering spectra. X-ray diffraction also reveals only Co_2Si. The reasons for the separate outcome in different experiments for Co remain to be established.

The Co_2Si thicknesses formed were measured by converting the energy widths defined by the half heights in the backscattering spectra to depth scales. In Fig. 3 the squared thicknesses of the formed Co_2Si layers after RTA at each temperature are plotted against the nominal RTA time. The good linearity of the plots indicates that Co_2Si grows as a square root of time by RTA and that its rate is limited by a diffusion process, as is the case in furnace annealing. The growth rate K of Co_2Si, defined as the square of thickness

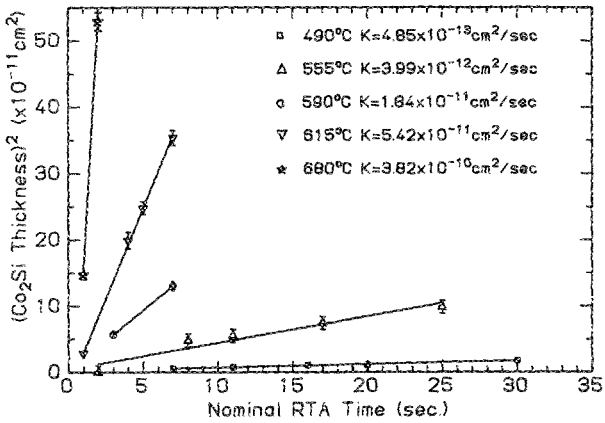

FIG. 3. Squared thickness of Co_2Si formed after RTA against the nominal RTA time.

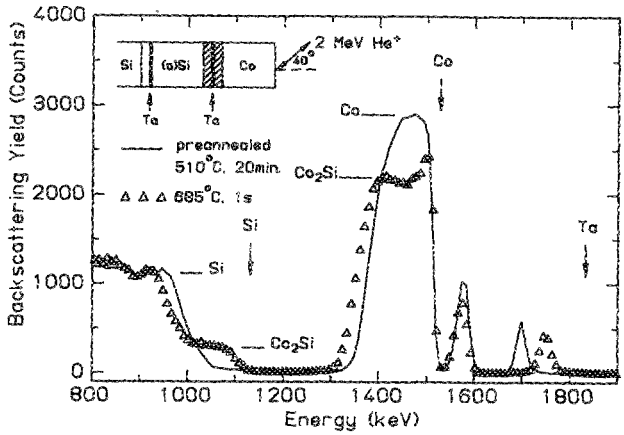

FIG. 5. 2-MeV $^4He^+$ backscattering spectra obtained from the preannealed sample (solid line) and after RTA at 685 °C for 1 s (triangle). The beam was incident at 40° from the sample normal; the scattering angle was 170°. The detection geometry is that described in the caption of Fig. 2. The hatched region represents the Co_2Si layer formed during preannealing.

divided by the annealing time at each temperature, is presented in the same figure.

Figure 4 shows the Arrhenius plot of Co_2Si growth rate K during RTA (square) and furnace annealing (circle). From the data, an activation energy of 2.2 ± 0.2 eV is obtained for the Co_2Si growth by RTA and 1.9 ± 0.2 eV for furnace annealing. The activation energy values are slightly higher than those obtained for furnace annealing on the single-crystal Si substrates, e.g., 1.65 ± 0.1 eV[18] on ⟨100⟩Si or 1.75 eV[21] on both ⟨100⟩ and ⟨111⟩Si. Usually, the activation energy of silicide formation is not changed by the types of Si substrates—crystalline or evaporated—as shown for Ni, Pd, Pt, and Cr silicides.[22] In the case of Co_2Si growth by furnace annealing, Lien *et al.*[19] report that the activation energy is 1.85 ± 0.1 eV on the evaporated Si, but 1.7 ± 0.1 eV on ⟨100⟩Si. This slight variation is believed to be due to different sample conditions, e.g., impurity content, microstructures of the substrate and the silicide, and the formation energy.[19] Our result for furnace annealing agrees with the report of Lien *et al.* on evaporated Si substrate. The activation energies obtained here for RTA and furnace annealing are also in reasonable agreement with each other. Since the primary concern in our work is with RTA, the furnace annealings were carried out for reference purpose only. However, as is seen in Fig. 4, the results for RTA and furnace annealing are consistent with a single common activation energy of 2.1 ± 0.2 eV. This shows that in Co_2Si formation, up to 680 °C, the RTA process is a simple projection of the standard thermal annealing process at a low temperature, up to the high-temperature range and with shortened annealing time, without significant change in formation kinetics.

B. Marker experiment

Typical backscattering spectra are shown in Fig. 5 for a sample after preannealing (solid line) and after RTA for nominally 1 s at 685 °C (triangle). The calculated signal heights of Co, Si, and Co_2Si are indicated by solid lines. The insert shows the configuration of a sample after preannealing for 20 min at 510 °C in a vacuum furnace. According to the kinetics data of Fig. 4, this heat treatment should have consumed all the Co film. Clearly, the additional complexity of the sample connected with the introduction of the markers does slow down the silicide growth. This does not necessarily invalidate the marker experiment. As long as the same compound forms as a result of a similar treatment, the transport

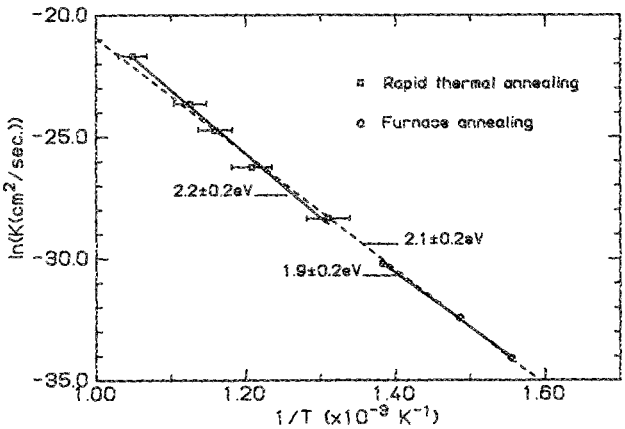

FIG. 4. Arrhenius plot of Co_2Si growth rate K. Squares and circles represent the results of RTA and furnace annealing, respectively. The data reflect an unchanged reaction mechanism over the whole temperature range investigated.

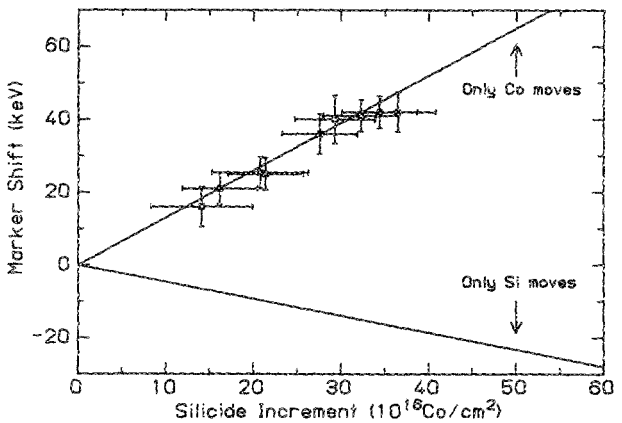

FIG. 6. Marker shifts, measured from spectra as shown in Fig. 5 with respect to the Ta reference signal, as a function of silicide increment.

mechanism is most likely to be the same. After RTA, the formation of Co_2Si and the associated marker movement are clearly observed in the spectrum. As in the case of the kinetics study, only one silicide is formed upon RTA. The formation of Co_2Si after RTA has been confirmed with x-ray diffraction. Note that in Fig. 5, the position of the Ta reference signal at about 1.58 MeV is fixed, confirming that the Ta reference layer is unaffected by RTA. Also note that as Co_2Si forms, the backscattering signal of the Ta marker shifts towards increasing energies.

From the backscattering spectra obtained after various RTA treatments, the amount of Co_2Si formation and the relative marker shifts were measured. The RTA temperatures ranged from 615 to 685 °C. Figure 6 shows these marker shifts associated with the formation of Co_2Si as a function of the silicide layer increment, i.e., the number of Co atoms per unit area added to the silicide layer. The solid lines correspond to marker motions calculated using the surface energy approximation for 100% atomic transport of either Co or Si during the formation of Co_2Si. Quite clearly, the results indicate that, up to 685 °C, Co is the dominant moving species in Co_2Si formation by RTA. The same results[16,23] have been reported for the formation of Co_2Si by conventional thermal annealing up to 450 °C.

IV. CONCLUSIONS

With a thin Co film deposited on an evaporated Si substrate, the growth kinetics and the identification of moving species during the formation of Co_2Si by RTA have been investigated up to about 680 °C. Until all Co is consumed, only one silicide, Co_2Si, grows upon RTA.

The growth of Co_2Si during RTA has a square root of time dependence, as in conventional thermal annealing. The Arrhenius plot of growth rate indicates that both RTA and furnace annealing activate basically the same reaction process. The common activation energy of Co_2Si growth over the whole temperature range investigated is 2.1 ± 0.2 eV.

The results of the marker study prove that Co is the only moving species involved in the atomic transport during the formation of Co_2Si by RTA as is the case for conventional thermal annealing at reduced temperatures for extended periods of time. The general conclusion is that over the whole range of temperatures and durations covered by RTA and conventional furnace annealing, Co_2Si forms by the same growth mechanisms.

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