Kinetics of NiAl$_3$ growth induced by steady-state thermal annealing at the Ni-⟨Al⟩ interface

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Substrates of large grained aluminum crystals were prepared by the strain annealing technique, and Ni films were vacuum evaporated on these substrates after an *in situ* sputter cleaning process. Upon thermal annealing of samples in vacuum, a laterally uniform growth of NiAl$_3$ is observed, starting from 330 °C, without any indication of boundary diffusion effects. The aluminide phase grows as (duration)$^{1/2}$ after an initial incubation period with an activation energy of 1.4 eV, i.e., $K = x^2/t = 0.387$ (cm^2/s)exp($- 1.4$ eV/kT) for 600 K $< T <$ 650 K. Impurities, either at the interface or inside the Ni film, retard this reaction.

I. INTRODUCTION

Al is the most widely used element for the metallization of Si integrated circuit. For VLSI (very large scale integrated) circuits, Al must generally be separated from Si by a barrier layer.[1] Transition metals or their compounds are good candidates for the barrier. How these metals react with Al upon subsequent thermal treatment is therefore of interest.

The early studies on thermal reaction between Al and transition metals quite naturally concentrated on deposited polycrystalline films of Al and transition metal.[2,3] It turns out that these reactions are dominated by grain-boundary processes which defy a simple analysis of the reaction processes.[4] To lessen this effect, one of the practical possibilities is to use a substrate of single-crystalline Al instead of evaporated Al film. Using such substrates will presumably result in the formation of planar layered reaction products with well-defined interfaces, as is the case for single-crystal Si substrates. If so, it is then also of interest to compare the formation processes of aluminides with those of silicides which are well known and documented.[5] There are difficulties with this approach. Aluminum has a thick native oxide layer (approximately 35 Å) which forms quite rapidly in air and hinders reactions with deposited metal films.[6] In addition, ⟨Al⟩ wafers of the quality and with a surface finish of common ⟨Si⟩ wafers are not commercially available. To prepare these is difficult because Al is soft. To resolve these problems we had recourse to Al sheets whose grains are a few millimeters to 1 cm in diameter [subsequently referred to as large grain ("⟨⟨Al⟩⟩") substrates], and *in situ* sputter cleaning just before evaporating the overlaid metal film, as will be described later in this paper.

The goal of this study is to investigate the thermal reaction of a transition metal film and Al without the complication of grain-boundary effects. The Ni/Al system was chosen for this first investigation. Our study also demonstrates how reactions can be investigated with minimal interference by grain boundaries where substrates are not conveniently available. This approach opens a door for investigations of thin-film reactions with other metal substrates, and will hopefully raise the appeal and pace of systematic investigations of this type as others follow the path chartered here.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

Large grains of Al can be readily grown in thin aluminum sheets by a strain annealing technique. The method depends on attaining a low density of nuclei for recrystallization and using a thermal treatment to enhance grain growth. The mechanisms and additional reference are described, for instance, in Ref. 7. The method applied here is to use many cold rolling and annealing cycles. The starting material was a 1.00-mm sheet of commercially pure aluminum (99.999%). Each rolling reduced the thickness by about 15% and was followed by annealing in air at 600 °C for 12–24 h. Grains can be visually examined after etching with warm (about 70 °C) NaOH of about 15 wt. % concentration. The cycle is repeated until a satisfactory grain size is obtained. Orientations of some large grains were determined by Laue x-ray diffraction.

These etched aluminum sheets were immersed in concentrated HF for about 10 min, rinsed in cold deionized water, and then blown dry with nitrogen before loading into an oil free evaporation system. Before the evaporation of the Ni film, the native oxide layer on the Al was removed by dc sputter cleaning, the typical conditions of which were the following: base pressure of 2–3×10^{-8} Torr; plasma pressure of 10^{-2} Torr of high-purity Ar purified by Ti sponge at about 700 °C; sputtering voltage of $- 5.5$ keV connected to the sample holder; sputtering rate of Al$_2$O$_3$ of 20 Å/s; duration of about 5–10 min without cooling. Immediately after terminating the sputtering the system was pumped down again to base pressure as fast as possible and Ni was deposited at a rate of about 15 Å/s by electron beam evaporation. The purity of the evaporation charge of Ni was 99.999%. The vacuum pressure rose to 3–4×10^{-7} Torr during the evaporation process. The thickness of the deposited Ni films was about 2000 Å. For comparison, films were sequentially deposited also on oxidized silicon wafers in the same pumpdown and with similar evaporation conditions. Thermal annealing was

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carried out in a vacuum furnace at a pressure below 4×10^{-7} Torr at various temperatures.

The atomic composition and thickness of the compound layer formed upon annealing were determined from 2-MeV He$^+$ backscattering spectra[8] to establish the growth kinetics of the thermal induced reaction. The phase formed was identified by glancing angle x-ray diffraction. Oxygen contamination at the interface was monitored by 3.05-MeV He^{++} resonance scattering.[6]

III. RESULTS

A. Large grain ("$\langle\langle Al \rangle\rangle$") substrates

As a typical example, the progressive formation of NiAl$_3$ at 356 °C for a Ni film on $\langle\langle Al \rangle\rangle$ measured by 2-MeV He$^+$ backscattering is shown in Fig. 1. It is clear to see that a well-defined phase grows uniformly in a layer-by-layer fashion. The slopes of the Ni and Al signals extrapolated to the reaction interfaces have a constant height ratio of Ni:Al = 1:3 $\pm$ 5% for various annealing times. These facts allow one to investigate growth kinetics of aluminides reliably and conveniently by backscattering spectrometry. X-ray diffraction patterns confirmed that the only detectable phase formed between 330 and 375 °C is NiAl$_3$, which is the most Al-rich compound known in the Al-Ni phase diagram. Annealing at 420 °C for 30 min was also performed. The reaction rate at this temperature was too fast for our techniques to characterize the growth kinetics. Even then, though, the compound phase formed was still NiAl$_3$. At that temperature, Ni$_2$Al$_3$ will be observed according to previous studies of the reaction of thin polycrystalline films.[9] It is probable that the second phase never appears in our case because the supply of Al from the $\langle\langle Al \rangle\rangle$ substrates is never exhausted; the $\langle\langle Al \rangle\rangle$ substrates are probably also much purer than evaporated Al films.

The kinetics of this reaction is reported in Fig. 2, where the square of the NiAl$_3$ thickness versus annealing time at different temperatures is plotted. The isothermal annealings were made with a number of samples prepared identically
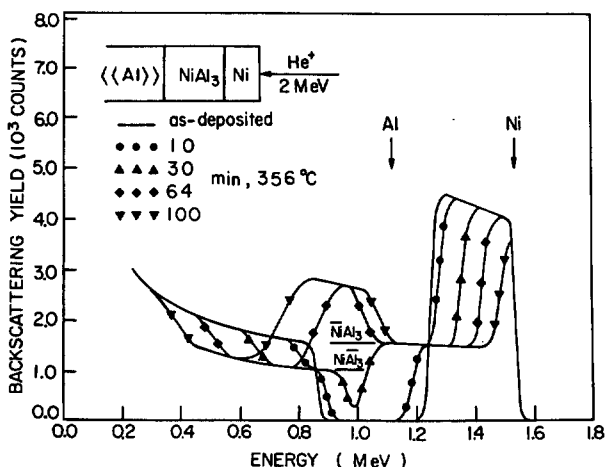
FIG. 2. The square of the grown layers of NiAl$_3$ vs annealing time for Ni/ $\langle\langle Al \rangle\rangle$ samples. [The vertical axis is calibrated in Ni atoms/cm^2 in the NiAl$_3$ layer formed. The actual thickness can be calculated by dividing that number through the density of a formula unit of NiAl$_3$, i.e., 1.707×10^{22}/ cm^3.]

and where each sample was annealed only once. Each set of data for certain annealing temperature follows a straight line with a time offset. This time dependence indicates a diffusion controlled kinetics. We verified that the reaction rate of Ni with $\langle\langle Al \rangle\rangle$ is reproducible, i.e., samples prepared, annealed, and analyzed separately yielded the same rate. An example is shown for 356 °C, where two sets of independent data ($\triangle$, $\blacktriangle$) follow almost exactly the same straight line. A separate preparation means here that different pieces of $\langle\langle Al \rangle\rangle$ sheets were used as substrate, and that the sputter cleaning followed by Ni evaporation was done at different times. The activation energy obtained from the Arrhenius plot of slopes of Fig. 2 is about 1.4 eV $\pm$ 0.1, as shown in Fig. 3, but we note that this value is based on an excursion of only 10% in $1/T$.

B. Single grain versus $\langle\langle Al \rangle\rangle$ substrates

The $\langle\langle Al \rangle\rangle$ sheets used throughout this study consist of many polyhedral grains of various orientations and about 1–2 mm in diameter. Each grain extends through the thickness of the sheet which is typically about 0.5 mm thick. As the beam spot of the incident He$^+$ for the analysis is about 3 mm in diameter, it samples several grains. The data presented in Figs. 1–3 are thus an average value taken over these few grains. Since the orientation of the individual grain can be one of the factors influencing the reaction kinetics, it is necessary to compare these average results with those obtained for only one single grain. For this purpose, an Al sheet with very large grains was chosen as a substrate. One grain was large enough to accommodate the beam spot. The orientation of this grain with respect to the substrate normal was determined by reflection Laue x-ray diffraction to be very close to $\langle 210 \rangle$. To assure a valid comparison, this large grain ($\langle\langle Al \rangle\rangle_0$) substrate and one of the others ($\langle\langle Al \rangle\rangle$) were pro-

FIG. 1. 2-MeV ^{4}He$^+$ backscattering spectra of Ni/$\langle\langle Al \rangle\rangle$ samples annealed at 356 °C for various durations showing the progressive formation of NiAl$_3$. (Normal beam incident; scattering angle of 170°.)
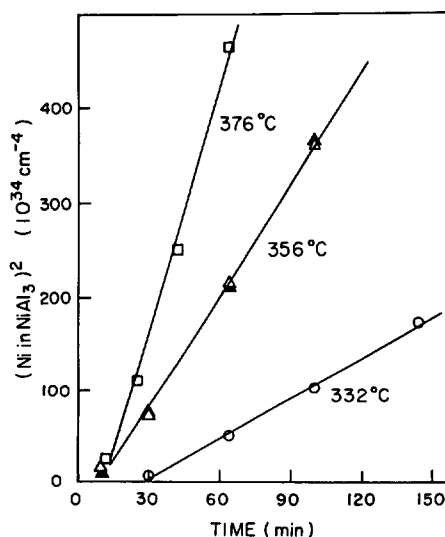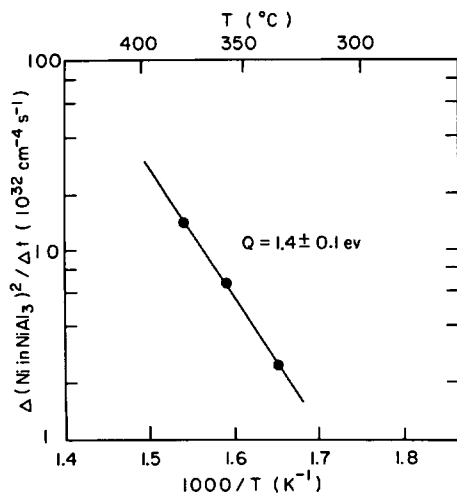
FIG. 3. Arrhenius plots obtained from the growth rates of NiAl$_3$ of Fig. 2.

FIG. 4. The samples compared are always prepared, treated, and analyzed simultaneously, with one intentional difference. (i) Samples $\bigcirc$ and $\bullet$ have a single-crystal Al substrate, while the substrate of samples $\triangle$ and $\blacktriangle$ contains several grains ("$\langle\langle$Al$\rangle\rangle$" substrate). (ii) Full symbols refer to a vacuum of 4×10^{-6} Torr during the Ni film evaporation, open symbols refer to a vacuum during Ni evaporation of 4×10^{-7} Torr. (iii) Different annealing procedures: the time dependencies indicated by the symbols $\triangle$, $\bigcirc$, $\blacktriangle$, and $\bullet$ were all obtained on one single sample each. The sample was annealed isothermally and subsequently analyzed at room temperature a number of times for an increasing total annealing duration as plotted on the abscissa. In contrast, the sample ∇ with an $\langle\langle$Al$\rangle\rangle$ substrate was heated only once. It reacts more rapidly than the comparable sample $\triangle$, but identically to those of Fig. 3 (dashed line).

cessed together (including sputter cleaning, evaporation of Ni film, and thermal treatment). The data shown in Fig. 4 were collected from these two samples. A sequence of isothermal annealings at 356 ± 1 °C was conducted with these samples by reannealing them a number of times. The abscissa of Fig. 4 is the total annealing time obtained by adding the last annealing duration to the previous total. That each group of lines in Fig. 4 has the same slope and systematically similar offsets indicates insignificant difference in the reaction behavior between several small grains and one large grain. This outcome proves that the reaction kinetics must be quite similar for several crystallographic orientations of Al. We conjecture that the kinetics may be the same for all low index planes. In the present case, the use of $\langle\langle$Al$\rangle\rangle$ sheets with discrete grains of various orientations instead of a single crystal is a shortcut that provides the main characteristics of a single-crystal reaction and yet economizes efforts in sample preparation.

The dashed line in Fig. 4 is that of Fig. 2 for 356 °C. There is a noticeable difference, although both sets of samples used for the two figures contained samples with polygrain $\langle\langle$Al$\rangle\rangle$ substrates. To clarify this discrepancy, one polygrain sample prepared with the second set used in Fig. 4 was annealed once at 356 °C for 30 min. The datum point (∇) for this sample coincides with the results of Fig. 2. Thus, the rates of Figs. 2 and 4 differ because of the different annealing procedures used. A multiple heat treatment of the same sample yields a slower reaction rate than a single heat treatment for the corresponding total annealing duration. This difference can have several causes. The multiple cycling of a sample from annealing temperature in vacuum to room temperature and atmospheric pressure may accelerate the contamination of the film. It is also possible that contaminations are introduced in the films during the backscattering analysis. Why the reaction should then still follow at $t^{1/2}$, as it does, is not clear.

How sensitive the reaction is to impurities can be seen in Fig. 4 also. This subject is discussed below.
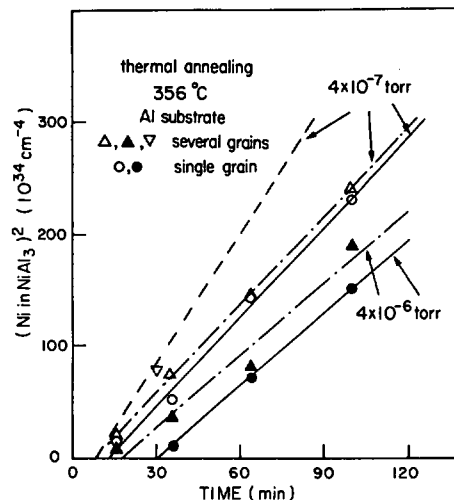
C. $\langle\langle$Al$\rangle\rangle$ substrates versus evaporated Al thin-film substrates

For comparison, samples of Ni/Al bilayers evaporated on oxidized Si substrates with the Ni film on top of the polycrystalline Al film were annealed in the same vacuum furnace. The backscattering spectra in Fig. 5 show that a tail develops at the back edge of the Ni signal already at 250 °C. With the temperature rising to about 275 °C, an additional step corresponding to NiAl$_3$ appears, while the level of Ni in the tail rises. The growth rate of the NiAl$_3$ layer on evaporated Al is less than that on $\langle$Al$\rangle$. At 330 °C, for instance, the rate on $\langle$Al$\rangle$ is almost twice that on evaporated Al. The advantage and importance of using a large grain substrate to investigate the Ni-Al reaction is clear when comparing the spectra of Figs. 1 and 5.

D. Impurity effects

It is well known that interfacial impurities can alter solid phase reactions, or even completely stop them.[10,11] Aluminum oxidizes rapidly in an ambient atmosphere and forms a native oxide of about 35 Å, (which is much thicker than the native oxide of silicon (about 15 Å)[12]. Therefore, oxygen must be considered a nefarious impurity in solid-state reactions of Al. In this work, the oxygen content at the Al/Ni interface was monitored by 3.05-MeV ^{4}He$^+$ resonance backscattering.[6] Figure 6 gives spectra of Ni/$\langle\langle$Al$\rangle\rangle$ sample before and after annealing for a case when an oxide layer was still present after an unsuccessful attempt at sputter clean-
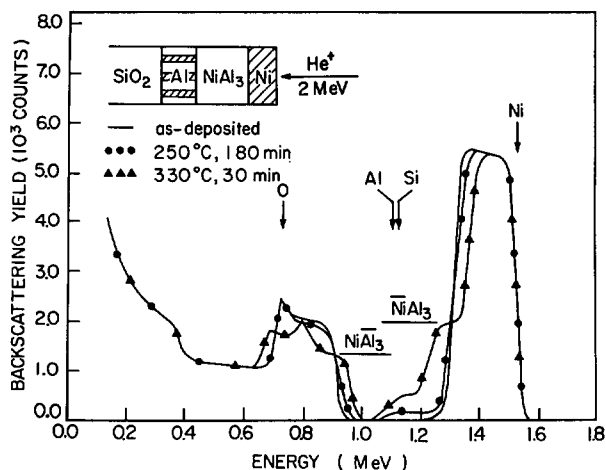
FIG. 5. 2-MeV ^{4}H$^+$ spectra of Ni/Al bilayer samples of which both layers were vacuum evaporated in a single pump down, as-deposited, and annealed at 250 and 330 °C. A rapid and localized interdiffusion, mainly of Ni into Al, occurs at 250 °C. At 330 °C both interfaces of NiAl$_3$ are of poor lateral uniformity. (Normal beam incident; scattering angle of 170°.)

ing. This oxide layer totally blocks the reaction even at a temperature as high as 400 °C. The layer contains the equivalent of 45 Å of Al$_2$O$_3$, which is thicker than a native oxide, showing that a poor sputter cleaning procedure aggravates rather than eases the interfacial impurity problem. After interfacial oxygen measurement on numerous samples, we conclude that a careful in situ sputter cleaning reduces the interfacial oxygen below the detection limit of the resonant scattering technique, which is equivalent to about two monolayers of oxide when the Ni overlayer is near 2000 Å thick. The interfacial cleanliness achieved by our sputtering technique is adequate to obtain accurately reproducible results with a laterally uniform growth of NiAl$_3$ (see Fig. 1). Even
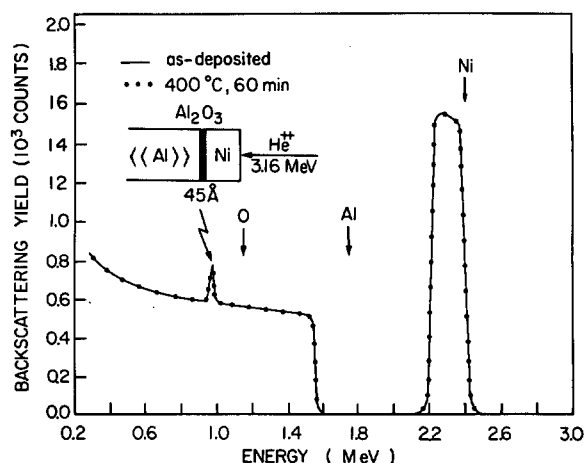

FIG. 6. 3.05-MeV ^{4}He^{++} resonant elastic scattering spectra of as-deposited and annealed samples. The oxygen signal near 1.0 MeV can be clearly seen. After annealing at 400 °C (which is much higher than the formation temperature of NiAl$_3$, see Figs. 1 and 2) there is no sign of a reaction. (Normal beam incident; scattering angle of 170°.)

so, some residual interfacial impurity is certainly still present. Evidence for that is contained in the incubation time of the kinetics plots of Figs. 2 and 4.

In addition to the interfacial impurities, the effect of bulk impurities contained in the evaporated film should also be taken into consideration. To observe their effect, Ni films were purposely deposited onto $\langle\langle$Al$\rangle\rangle$ substrates in a poor (about 4×10^{-6} Torr) and a better (about 4×10^{-7} Torr) vacuum. Base pressure and sputter cleaning conditions were the same for both cases. Both samples were then annealed simultaneously at 356 °C for increasingly longer (additive) durations. The results are shown in Fig. 4. Clearly the reaction rates, i.e., the slopes of lines in Fig. 4, of the samples with Ni films prepared in poor vacuum are noticeably lower (by about 20%) than those of the better samples. Oxygen profiles in the Ni films for both types of samples have been carefully measured by the O$^{16}(\alpha,\alpha)$O^{16} technique with the incident beam energy varied step by step. No oxygen was detectable. In the case of the Ni film, the detection limit is about 1 at. %. Thus, it turns out that aluminide formation of a Ni film on $\langle\langle$Al$\rangle\rangle$ substrates is sensitive to oxygen concentrations below 1 at. %, or that other impurities, not monitored here, also alter rate of reaction.

IV. COMPARISONS WITH OTHER DATA

Our results on $\langle$Al$\rangle$ crystals agree with earlier reports in that the growth rate of the NiAl$_3$ phase is diffusion limited with a parabolic time dependence, whatever processes were used, including sample preparation and isothermal annealing procedure. Janssen and Rieck[13] formed Ni/Al samples by hot dipping of pure nickel disks in an aluminum melt of 700 °C in nitrogen atmosphere and then annealed in hydrogen or argon at atmospheric pressure. Baglin and Poate[11] used evaporated thin films of Al and Ni on SiO$_2$ for their study.

While NiAl$_3$ is reported to grow as $t^{1/2}$ in each case, the reaction rate constants $K = x^2/t$ differ hugely from each other. In our case, K can be expressed as $K = 0.387$ exp $- (1.4\,\mathrm{eV}/kT)$ cm^2/s for the clean Ni/$\langle\langle$Al$\rangle\rangle$ samples in the range 330 °C $< T <$ 380 °C, using a bulk density of 1.707×10^{22} NiAl$_3$ units/cm^3 (Ref. 14); it follows that $K(275$ °C) and $K(610$ °C) are 1.40×10^{-13} cm^2/s and 3.99×10^{-9} cm^2/s, respectively, assuming that the above expression is still applicable. From BS spectra of Baglin's paper, we estimate a reaction rate constant of $K(275$ °C) of 5×10^{-15} cm^2/s. Janssen reports a K of about 10^{-11} cm^2/s at 610 °C. Both values are several orders of magnitude smaller than ours. On the other hand, the reaction rate for our substrates made of polycrystalline thin films is only half that of $\langle\langle$Al$\rangle\rangle$ substrates. Therefore, we believe that the big difference in reaction rates is attributable to the purity of samples and the cleanliness of interfaces, since the reaction is very sensitive to impurities, as shown in Fig. 4.

It should also be pointed out that the temperature required to initiate the reaction of Ni on a single-crystalline Al substrate ($\langle\langle$Al$\rangle\rangle$) is about 70 °C higher than that required for a polycrystalline Al film. It is conceivable that this is caused by the initial presence of a residual oxide layer at the interface. This point of view is also supported by well-known

silicide formation studies.[15] The *in situ* sputtering procedure used here is an effective cleaning technique, but a complete removal of impurities, especially oxygen, cannot be expected in a vacuum such as that used here.

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