RE-EMITTED POSITRON SPECTROSCOPY OF COBALT AND NICKEL SILICIDE FILMS

B.D. Wissman, W.E. Frieze, and D.W. Gidley
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

ABSTRACT

The techniques of re-emitted positron spectroscopy (RPS) have been employed in the first systematic investigation[†] of the positronic properties of the various stoichiometric phases (M_2Si, MSi, and MSi_2) of Co and Ni silicide films grown *in situ* on Si substrates. The positron work function is found to be negative for all of the different phases; thus implanted positrons may be re-emitted. The energy of the re-emitted positrons is found to have a surprisingly large variation for the different phases. This feature should provide the image contrast necessary to observe each phase on a microscopic scale using the positron re-emission microscope (PRM). The positron deformation potential, $E_d^+ \equiv V(\partial\Sigma/\partial V)$, was determined for $CoSi_2$ films; it can be used to estimate the size of the positron diffusion constant, which is found to be comparable to that of other metals. Thus the short positron diffusion length (of order 150 Å) determined from depth-profiling measurements of $CoSi_2$ films must be a result of positron trapping in either the film or at the interface with the Si substrate. RPS results considered as a function of film thickness support the conclusion that defects in the film (misfit dislocations and/or vacancies) represent the major source of positron trapping.

INTRODUCTION

There is a great deal of interest in the formation of metal silicide films due to their many device applications, such as Schottky barriers, ohmic contacts, low resistivity interconnects, and metal base and permeable base transistors.[1,2,3] A number of the metal silicides are known to grow epitaxially, and of these, $CoSi_2$ and $NiSi_2$ are of particular interest due to their small lattice mismatches with Si (1.2 % and 0.4 %, respectively[4]). These small lattice mismatches permit the growth of silicide films with nearly perfect epitaxial structure on Si substrates, which, under certain conditions, may be pseudomorphic.[1,5,6] In addition to their technological applications, the possibility of growing silicide films which have nearly perfect interfaces with Si substrates makes them ideal systems in which to study the basic physics of metal-semiconductor junctions.[4] Such films are attractive systems for studying the diffusion, drift[7] , and trapping of positrons in the vicinity of the Schottky *well* and the associated depletion region. However, very little is known about the properties that determine positron transport in these materials. The only study[8] is of $CoSi_2$, in which it was discovered that a thin film grown on a Si(111) substrate has a negative positron work

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function. $CoSi_2$ therefore re-emits positrons; thus the techniques of re-emitted positron spectroscopy (RPS) can be applied to this and other silicide systems.

In RPS one measures the energy distribution of positrons which are re-emitted after being implanted with incident energies of order several keV, thermalizing, and subsequently diffusing back to the surface. Due to the presence of contact potentials, the energy of elastically emitted positrons is determined[9] by a parameter Σ, where

$$\Sigma \equiv \mu^- + \mu^+ = -\ (\ \phi^- + \phi^+\ ). \tag{1}$$

Here μ^- and μ^+ are the bulk electron and positron chemical potentials, and ϕ^- and ϕ^+ are the electron and positron work functions, respectively. Note that Σ (sometimes referred to as the positron affinity) is negative, and that a more negative value indicates a stronger affinity of a particular material for positrons.[10] Positrons which have been implanted into a multilayer structure may be re-emitted with well-defined energies which are characteristic of each material. By identifying the peak energy and any shifts thereof, RPS can be used to probe heterogeneous growth systems, e.g. interdiffusion alloying[9] and pseudomorphism.[11] In particular, in the present work we can observe the thermal reaction of Co and Ni layers deposited on Si to form the various silicide phases. RPS spectra are investigated as a function of: the initial thickness of the metal overlayer, the annealing/reaction temperature, and the incident positron energy.

EXPERIMENTAL TECHNIQUE

Co and Ni silicides were grown *in situ* by thermal reaction of thin (5 – 200 Å) Co and Ni films which had been deposited by evaporation from a heated W filament onto Si substrates which were at room temperature. All work was performed in a UHV surface analysis chamber, with base pressure 1×10^{-10} Torr. The background pressure remained below 2×10^{-7} Torr at all times during the deposition and annealing. Silicide growth was monitored by both Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), with the various silicide phases obtained by varying the annealing time and temperature.[12] The substrates were cleaned by sputtering with 1 – 2 keV Ar ions, followed by a quick (< 30 sec) heat to 1100 – 1200 °C. Samples cleaned in this manner exhibited good LEED patterns, and had negligible surface contaminations of C. In the case of the (111) substrates, the 7x7 surface reconstruction was typically observed.

RPS studies were done using a variable energy (0.5 – 4.0 keV) monoenergetic beam. At these beam energies the mean implantation depth[13] $\bar{z}$ varies from approximately 25 – 750 Å. The energies of the re-emitted positrons were measured with a double-pass cylindrical mirror analyzer operating in a constant pass-energy mode.[9] The value of Σ is determined by the energy of the elastic peak relative to that of a Ni(100) reference crystal, with Σ_{Ni} taken to be -3.8 eV, as discussed below. The absolute energy scale is calibrated by defining

ϕ^- (and hence the zero positron energy cutoff) of the clean Ni(100) crystal to be 5.2 eV.[14] $|\phi^+|$ is determined by the energy difference between the elastic peak and the corresponding zero energy cutoff, minus a correction due to the resolution of the analyzer. On an absolute scale our measurements of ϕ^+ and Σ are uncertain at the ± 0.1 eV level. However, by measuring Σ relative to a reference crystal, the relative values of Σ can be determined to an accuracy of approximately ± 20 meV. Relative values of ϕ^- may be determined to an accuracy of approximately ± 50 meV. The clean Ni(100) reference crystal is found (after a resolution-shift correction of 0.25 eV) to have $\phi^+ = -1.4$ eV, therefore from Eq.(1) $\Sigma_{\mathrm{Ni}} = -3.8$ eV.

RPS OF SILICIDES

A. Ni Silicides on Si(100)

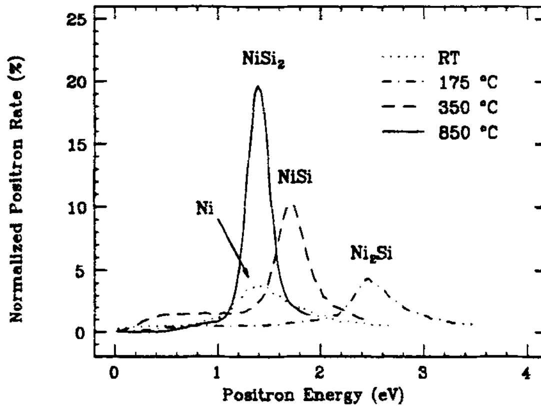

Figure 1: RPS Spectra of 50 Å Ni/Si(100). The spectra, acquired at RT using 1 keV positrons, show the progression from un-reacted Ni (as deposited at RT), to Ni_2Si, to NiSi, to $NiSi_2$ with increased annealing temperature. The spectra are normalized such that the vertical scale represents the peak rate as a fraction of the rate (at 1 keV) of the Ni(100) reference crystal.

A Ni film of thickness approximately 50 Å was deposited on a n-Si(100) substrate ($\rho \approx 10\ \Omega \cdot \mathrm{cm}$) and annealed at progressively higher temperatures (as noted in Fig. 1) to produce the different silicide phases: Ni_2Si, NiSi, and $NiSi_2$, in order of increasing reaction temperature. Assuming uniform layer growth, this amount of Ni would produce silicide film thicknesses of approximately 75, 100, and 175 Å, respectively.[15] The corresponding mean implantation depths for 1 keV positrons range from approximately 50 – 80 Å. At annealing temperatures below 175 °C the RPS spectrum indicated the presence of only un-reacted Ni,

consistent with AES. A distinct Ni_2Si peak appeared after annealing at 175 °C. After annealing at 250 °C a distinct NiSi peak appeared. The transition to $NiSi_2$ began after reaction at 650 °C, with LEED indicating a highly-ordered surface. After annealing at 850 °C a well isolated peak corresponding to $NiSi_2$ was observed. All three Ni silicide phases are clearly distinguishable in Fig. 1, and it is interesting to note that their peaks are equal or higher in energy than that of pure Ni (i.e. despite the fact that Σ_{Si} has a low value, the Ni silicides all have $\Sigma \geq \Sigma_{Ni}$).

By increasing the incident positron beam energy, and hence the mean implantation depth, we can sample progressively deeper below the surface. This simple form of depth-profiling was used to demonstrate the transition from a NiSi film of thickness approximately 100 Å to a $NiSi_2$ film of thickness approximately 175 Å as the annealing temperature of a 50 Å Ni film was increased from 650 °C (Fig. 2) to 750 °C. As can be seen in Fig. 2, the slightest hint of $NiSi_2$ is observed for the lowest implantation energy ($\bar{z} \approx 25$ Å), indicating the presence of $NiSi_2$ near the surface, consistent with AES and LEED observations. After annealing at 750 °C, a 4 keV spectrum ($\bar{z} \approx 750$ Å) shows a NiSi peak, but the spectrum acquired using less penetrating 1 keV incident positrons ($\bar{z} \approx 75$ Å) shows only a slight mounding at that energy, indicating the presence of deep-lying NiSi, thus indicating that the the final transformation occurs deep in the film.

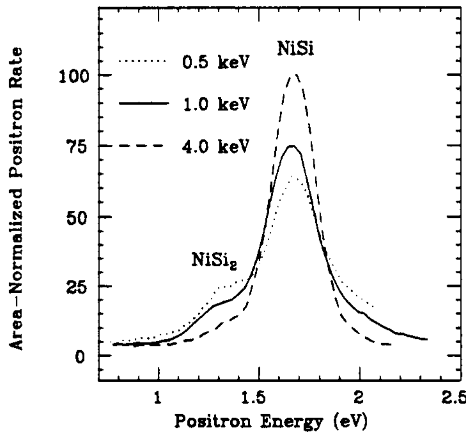

Figure 2: RPS Spectra as a Function of Incident Energy. RPS spectra of a 50 Å Ni film annealed at 650 °C. The spectra, acquired at RT, are normalized to equal areas.

B. Co Silicides on Si(111)

A Co film of thickness 100 Å was deposited on a n-Si(111) substrate ($\rho \approx 0.13\ \Omega \cdot \mathrm{cm}$) and annealed at progressively higher temperatures to produce the different silicide phases: Co_2Si, CoSi, and $CoSi_2$, in order of increasing reaction temperature. Assuming uniform layer growth, this amount of Co would produce silicide film thicknesses of approximately 150, 200, and 350 Å, respectively.[15]

The corresponding mean implantation depths for 1 keV positrons range from approximately 50 – 80 Å. At annealing temperatures below 300 °C the RPS spectrum indicated the presence of only un-reacted Co, consistent with AES. After annealing for 5 minutes at 300 °C the RPS spectrum had distinct Co and Co_2Si peaks, plus a mound at the energy corresponding to CoSi. An isolated Co_2Si peak was never seen - it was always accompanied by Co and CoSi peaks. This was also the case for silicide films grown from Co films of initial thicknesses of 150 and 200 Å, consistent with the observation that the growth of Co_2Si and CoSi occurs simultaneously.[16,17] Further annealing at 300 °C resulted in a transition from Co_2Si to CoSi, with the size of the CoSi peak increasing relative to that of Co_2Si with increasing annealing time. After annealing for 10 minutes at 350 °C the Co_2Si peak disappeared, leaving a lone CoSi peak. The transition from CoSi to $CoSi_2$ occurred after annealing near 450 °C. At reaction temperatures above 550 °C, a lone peak corresponding to $CoSi_2$ was observed, with LEED indicating a highly-ordered surface.

C. Discussion of Results

The results of the above-mentioned spectra are presented graphically in Fig. 3. All of the different silicides are found to have negative ϕ^+. In all cases the Σ values are large enough that the silicide films present an energy barrier of several electron-volts to positrons which have thermalized in the Si substrate (and thus would not be appropriate as electrical contacts for a field-assisted positron moderator). Of course, if the predicted[10] value of Σ_{Si} shown in Fig. 3 is correct, then it is very unlikely that any metal contact would be suitable.

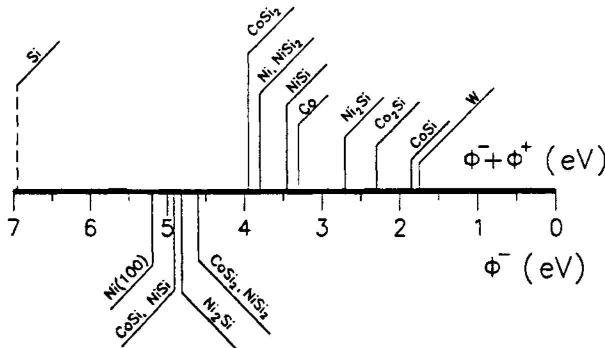

Figure 3: Measured RPS Peak Energies and Cutoffs. The value for Si is a theoretical prediction.[10] The energy scale is reversed so that positron energy increases to the right. The absolute energy scale is set by defining ϕ^- for Ni(100) to be 5.2 eV.[14]

Several other interesting features can be seen in Fig. 3. There is a relatively wide variation in Σ for the different silicides, particularly for the Co silicides. It is this property that allows each phase to be very easily distinguished in the

RPS spectra. There is a correspondingly large variation in $|\phi^+|$ (0.6 - 3.0 eV) with relatively little variation in ϕ^- (4.5 - 4.9 eV). In addition, the value of Σ is surprisingly large compared with that of the pure metal. The Ni silicide peaks all have Σ equal to, or greater than, that of pure Ni even though they rank in order of increasing Σ from Si-rich to Ni-rich. Naively, one might have expected (on the basis of alloying results[9]) that the silicides would lie between Si and Ni in Fig. 3, with the Ni-rich phase approaching Ni from the left. This is clearly not the case, and thus it would be interesting to have detailed calculations of μ^- and μ^+ for the silicides(as per Ref. 10 for the elements). Another interesting feature is the difference in the ordering of the Σ values for the Co silicides as opposed to the Ni silicides. This may be explained by the fact that while both metal-rich phases have the $PbCl_2$ structure, and both Si-rich phases have the CaF_2 structure, the structures of the intermediate phases are different; NiSi has the orthorhombic MnP structure, whereas CoSi has the cubic FeSi structure.[15] As a result, the atomic density of CoSi is slightly larger than that of NiSi, which may account for the fact that its Σ value is larger (i.e. less negative) than that of the other silicides. Nonetheless, we were surprised to find such a large value of Σ (-1.85 eV), and such a large and negative ϕ^+ (-3.02 eV) for CoSi, comparable to such extreme values as those for W.

Another feature, clearly evident in Fig. 1, is that the re-emitted positron yield in the elastic peaks of all of the silicides are small, ranging from approximately $4 - 20$ % for the Ni silicides at 1 keV (and correspondingly $1 - 10$ % for the Co silicides), where the yields are given as a fraction of the elastic peak yield (at 1 keV) of a clean, well-annealed, single crystal Ni reference. The total (energy-integrated) yield at 1 keV of re-emitted positrons shows much less variation, ranging from approximately 15 % for the metal-rich and intermediate phases to $25 - 30$ % for the Si-rich phase, where the yields are given as a fraction of the total yield (at 1 keV) of the Ni reference crystal. These results are not surprising for the metal-rich and intermediate phases since the non-epitaxial nature of their growth (indicated by the lack of a LEED pattern) presumably leads to highly defective films. The low peak rates relative to that of the Ni reference indicate that the positrons are emitted with an angular distribution that is much broader than the angular acceptance of our energy analyzer, thus suggesting a rough or faceted surface. The higher re-emission rates from the Si-rich phase are certainly due to their better epitaxy. Nevertheless, their relatively low total yields may well be due to the presence of misfit dislocations or other positron-trapping defects, as discussed below.

To further investigate trapping defects, the total yield of re-emitted positrons from $CoSi_2$ films (thickness ≈ 700 Å) grown by the deposition of a 200 Å Co film, with subsequent annealing at 600 °C and 850 °C are shown in Fig. 4 as a function of incident positron energy. Note that the total yield drops rather sharply with increasing incident energy, and hence implantation depth. The data were fitted to a function of the form[18] $f = f_0 \, [1 + (\frac{E}{E_0})^{1.6}]^{-1}$. The fits yield E_0 values of 1.30 keV and 1.36 keV for the 600 °C and 850 °C data, respectively. These low values indicate that the film has a very short positron diffusion length, of order 150 Å. This is in reasonable agreement with the result obtained by Gullikson *et al.* for a film grown by MBE.[8] There are either positron-trapping defects (misfit dislocations and/or vacancies) in the film, or the Si interface/Schottky

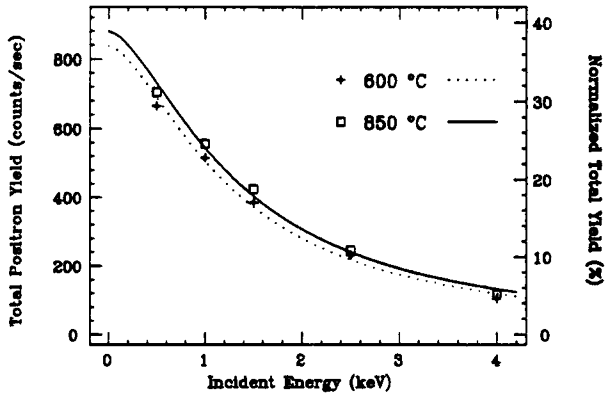

Figure 4: Total Positron Yield vs. Incident Energy. Total yield at RT from a Co film annealed at 600 °C and 850 °C to form $CoSi_2$. The right-hand scale represents the total yield as a fraction of the yield (extrapolated to zero incident energy) of the Ni(100) reference crystal. The dotted and solid curves represent fits to the 600 °C and 850 °C data, respectively.

well is trapping most of the positrons in the film. There is evidence for positron-trapping defects, as will be discussed in the following sections.

POSITRON DEFORMATION POTENTIAL OF $CoSi_2$

The positron deformation potential relates changes in Σ to variations in the bulk atomic density[10] , and is defined as $E_d^+ \equiv V\ (\partial\Sigma/\partial V)$. The temperature dependence of Σ was measured for several $CoSi_2$ films grown by depositing Co films of thickness 100 - 200 Å on Si(111) substrates and annealing at 850 °C. This temperature dependence appears in the RPS spectrum in the form of a shift in the elastic peak energy. The peak energy was measured as a function of temperature as the samples were radiatively heated. Incident positrons of energy 1 keV were used. The peak shift was found to be linear in the range from 25 – 275 °C, with the slope $d\Sigma/dT = -0.22 \pm 0.03$ meV/ K. This value can be related to E_d^+ using the linear coefficient of thermal expansion, α.[11] Using $\alpha = 10.1 \times 10^{-6}\ K^{-1}$,[19] the measured temperature dependence then yields $E_d^+ = -7.3 \pm 1.0$ eV, where the error quoted is due to the statistical error in determining $d\Sigma/dT$.

The deformation potential is a measure of the strength of the positron-phonon coupling, and therefore may be used to estimate the size of the positron diffusion constant, D^+, due to acoustic phonon scattering .[20] The diffusion constant is directly related to the positron diffusion length[13] , which determines many of the positron transport properties of a material. Using the measured values of the elastic constants[21] , and taking the effective mass of the positron to be

$m^* = 1.5\ m_e$, which represents a reasonable compromise between theoretical and experimental estimates for most materials[20], the above value of E_d^+ yields the relatively large value of 2.9 cm^2/sec for D^+ at 300K (typical metals have diffusion constants of order $0.1 - 1.0\ cm^2/sec$[13]). In the absence of positron-trapping defects, the resulting positron diffusion length is of order several thousand Angstroms, comparable to that of Ni. Thus the relatively low yield of re-emitted positrons from the silicides indicates that a significant number of positrons are trapping. We will consider this point further in the following section.

ULTRATHIN $CoSi_2$ FILMS

As mentioned earlier, all of the silicides exhibit relatively small re-emitted positron yields. We concluded earlier that in all likelihood the metal-rich and intermediate phases have a high density of open-volume defects that trap positrons, but that the situation for the Si-rich phase was less clear. In order to distinguish trapping in bulk defects from trapping at the Si interface/Schottky well, we measured the positron peak rate and total yield of ultrathin $CoSi_2$ films grown by a multiple-step deposition and 850 °C reaction technique. Co films were deposited with rates of order 0.2 Å/sec, with the background pressure in the chamber remaining below 2×10^{-9} Torr at all times during the deposition and annealing. These data (acquired using 1 keV incident positrons with $\bar{z} \approx 80$ Å) are plotted in Fig. 5, as a function of the initial Co film thickness. We find that both the peak rate and total yield approach the thick film (700 Å) values of 8 – 10 % and 25 – 30 %, respectively, for Co film thickness of order 40 Å (corresponding to 140 Å $CoSi_2$ thickness). This is consistent with a *bulk* diffusion length of order 150 Å (in agreement with our depth-profiling results). It is not consistent with a long *bulk* diffusion length (e.g. no bulk defects) and trapping only at the interface. If this were the case, a sizable increase in re-emission (of order 50 %) would be expected when the film thickness is increased from 140 Å to 700 Å. Thus the Si interface/Schottky well is not the major source of positron trapping, and we therefore conclude that the positrons are mainly trapping in misfit dislocations/and or vacancies.

CONCLUSION

All of the different phases of Co and Ni silicides re-emit positrons, with $|\phi^+|$ ranging from 0.6 to 3.0 eV. As there is little variation in ϕ^-, the parameter Σ (which represents the positron energy level in a particular material) therefore also has a comparably large variation. In general, Σ increases with increasing atomic density, which in turn tends to decrease with the silicide reaction temperature as the film is transformed from the metal-rich to the Si-rich phase. The rate of positron re-emission in the elastic peak increases in going from the metal-rich to the Si-rich phase. This feature, together with the widely separated and thus easily distinguishable peaks in the RPS spectra for each silicide phase, should provide the necessary image contrast for observing each phase on a microscopic scale using the positron re-emission microscope (PRM).[22,23] Depth-profiled PRM images may provide a unique perspective on the dynamics of the

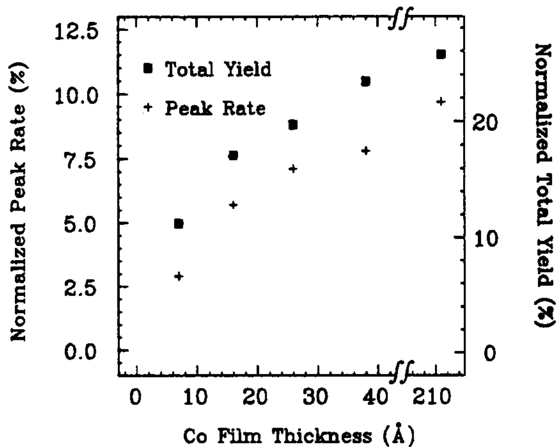

Figure 5: Peak Rate and Total Yield vs. Co Film Thickness. $CoSi_2$ films were grown by sequential steps of Co deposition followed by annealing at 850 °C. The peak rate and total yield (at 1 keV) are expressed as fractions of those (at 1 keV) of the Ni(100) reference crystal.

silicide growth as it proceeds through the various phases by diffusion and/or nucleation. In the particular case of $CoSi_2$ films, a PRM with the predicted lateral resolution of order 10 Å[22,23] could readily be used to observe the formation of non-emitting Si pin-holes, which have lateral dimensions larger than 100 Å.[4] Such pinholes play a strong role in determining the electron transport properties of Si/$CoSi_2$/Si metal and permeable base transistors.[2,3]

Our measurement of the positron deformation potential, along with a reasonable estimate of the positron effective mass, can be used to deduce that the positron diffusion constant in $CoSi_2$ is comparable to that of typical metals. Thus the short positron diffusion length (of order 150 Å) determined in depth-profiling measurements cannot be attributed to a small diffusion constant. Positrons must be trapping in the Schottky well, or in defects in the film or at the interface with the Si substrate. Our RPS measurements, considered as a function of film thickness, distinguish defects in the film (presumably misfit dislocations and/or vacancies) as the dominant source of positron trapping. We cannot distinguish any significant trapping at the Si interface/ Schottky well. It would be interesting to employ depth-profiled Doppler broadening spectroscopy[13] on a thick $CoSi_2$ film to provide further confirmation of this conclusion.

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