PHYSICAL REVIEW B VOLUME 36, NUMBER 14 15 NOVEMBER 1987-I

Auger-electron-spectroscopy analysis of a plasmon loss in palladium silicide formed from Pd deposits on silicon

R. Anton, U. Neukirch, and M. Harsdorff
Institut für Angewandte Physik, Universität Hamburg, Jungiusstrasse 11, D-2000 Hamburg 36,
Federal Republic of Germany
(Received 20 January 1987)

Auger-electron spectra of Pd_2Si formed by reactive interaction of ultrathin Pd deposits with clean and native oxide-covered Si substrates at elevated temperatures exhibit an additional peak at about 313 eV, which is not present in spectra of Pd alone. A clear correlation of the peak intensity with segregation of Si was found, leading to the conclusion that its origin is a plasmon loss of about 17 eV in the Si overlayer being excited by Pd Auger electrons of energy 330 eV.

I. INTRODUCTION

The formation of palladium silicide on Si substrate surfaces has repeatedly been studied in the past because of potential device applications and for general interest in the basic understanding of the formation and properties of metal-semiconductor interfaces. Various analytical techniques have been applied to this system, such as Auger-electron spectroscopy (AES), ultraviolet photoemission spectroscopy (UPS), low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), transmission electron microscopy (TEM), or electric measurements.[1] The silicide reaction has not only been studied on clean silicon substrates but also in presence of oxide interlayers.[2,3] There exists general agreement that the only phase being formed is Pd_2Si. However, indications for a more gradual increase of the concentration of Si, or Si enrichment, at the Si-silicide interface had been found by electron spectroscopic methods,[4] although TEM lattice imaging suggested locally sharp boundaries.[5] Moreover, Auger and photoelectron studies revealed that a thin segregated overlayer of Si develops on the silicide when the temperature is raised to above 200 °C.[6] These findings also apply to the case of a thin oxide interface being present before the deposition of Pd.[3] However, this leads to a different morphology and different degree of epitaxial order of the silicide.

The electronic structure of Pd_2Si has also been investigated. Electron-energy-loss spectra revealed a shift and broadening of the Si plasmon loss from 17 to 24 eV, which was attributed to the higher electron density in the conduction or valence band of the silicide when compared with Si.[4] In AES, a characteristic splitting of the Si *LVV* transition was attributed to the formation of Pd_2Si.[7] In some studies, an additional peak at about 20–24 eV below the main Auger line of Pd at 330 eV has been noticed, yet not identified.[7]

We have investigated the intensity and width of this peak during systematic studies of the Pd silicide formation under various reaction conditions, with and without an intermediate native oxide layer, especially with regard to Si segregation at the surface of the silicide. It will be shown that there exists a correlation between the peak intensity at about 313 eV and the extent of Si segregation.

II. EXPERIMENT

Si wafer material with orientations (111) and (100) was cut into pieces of 1×1 cm^2 size and placed in a UHV chamber equipped with metal deposition, AES, and RHEED facilities. Cleaning by Ar-ion bombardment at 900 °C resulted in reconstructed 2×1 surfaces on Si(100) and 7×7 surfaces on Si(111) as detected by RHEED. Some samples were taken as received with a native oxide coverage of about 2 nm thickness. These were heated to 600 °C in vacuo for several hours to remove a carbon contamination. Virtually no change of the silicon and oxygen Auger peak heights occurred during this treatment. Pd films with thicknesses up to 6 nm were deposited onto the substrates at temperatures from 25 to 600 °C. Auger electron spectra and RHEED patterns were recorded during various stages of deposition and/or postdeposition annealing. The primary electron energy was 50 keV, and the angle of incidence was a few degrees with respect to the substrate surface. The axis of the electron spectrometer (cylindrical mirror analyzer) was oriented at 90° off the incident beam direction. The resolution in energy was 1%. Further details have been described elsewhere.[3,8]

III. RESULTS

A. Clean Si substrates

Figure 1(a) shows an Auger spectrum which was obtained after deposition of Pd with 0.35 nm thickness on clean Si(111) at room temperature. The characteristic splitting of the Si *LVV* transition with peaks at 79, 85, 90, and 94 eV has clearly developed, which is usually attributed to the formation of Pd_2Si. However, the RHEED pattern only exhibited diffuse rings indicating a polycrystalline structure with small crystallite sizes. In

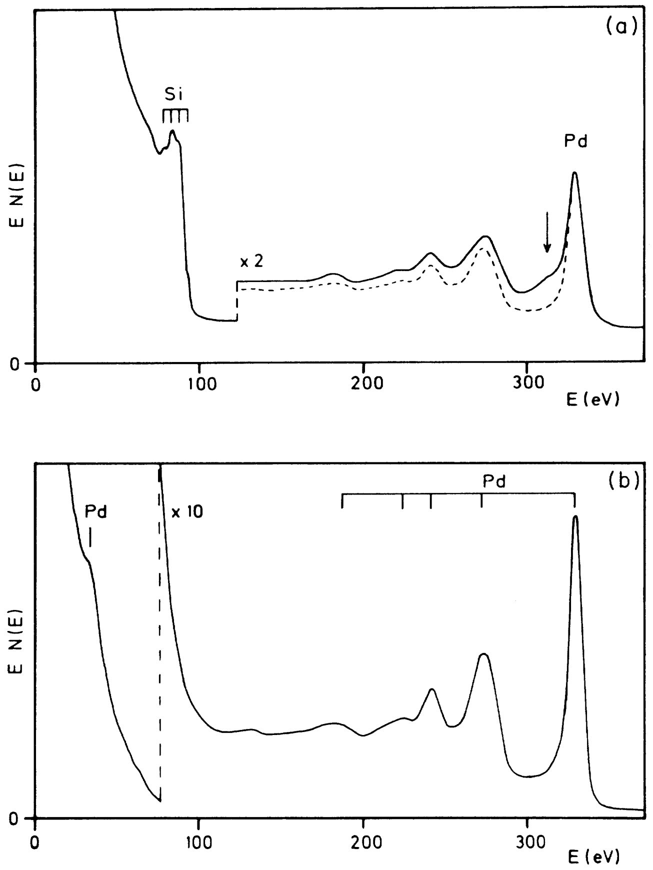

FIG. 1. (a) Smoothed secondary-electron spectrum of Pd_2Si formed by deposition of Pd of 0.35 nm equivalent thickness on Si(111) at room temperature. The broken curve represents a normalized spectrum of a thick film of Pd. Note the enhanced background at the low-energy tails of the Pd Auger lines. The arrow marks an additional peak at about 313 eV, which is not present in the spectrum of Pd. (b) Spectrum of a thick film of Pd.

addition, a broad peak appeared at about 313±1 eV, which is not found in spectra of thick Pd films, as is shown in Fig. 1(b) for comparison. It is also apparent from Fig. 1 that the background intensity at the low-energy tails of the Pd Auger lines at 120, 185, 220, 235, 276, and 330 eV is somewhat enhanced by silicide formation. This indicates that the Pd Auger electrons suffer stronger inelastic losses in the silicide than in Pd before being emitted from the surface of the sample. Therefore, the feature at around 313 eV appears to be a superposition of a small peak on a monotonic background, which is increased by the formation of silicide.

The intensity of this peak as well as the background enhancement was found to decrease during further deposition of Pd, as a film of unreacted metal developed when its thickness exceeded about 1.2 nm, as seen by RHEED observations. Whether the metal film contained some Si in solution, as may be suspected, could not definitely be verified, since ion sputter profiling may have resulted in an enhancement of the silicide reaction (see the remarks in Sec. III C). Similar results in all respects were found on clean Si(100) substrates.

When the deposition of Pd was performed at elevated temperatures, the development of the Si *LVV* splitting as well as of the additional peak at 313 eV could be followed to much higher amounts of deposited Pd. This is illustrated in Fig. 2(a) for the case of 3.5 nm of Pd deposited at 230 °C on Si(111). An even stronger enhancement of the background (by roughly 50% compared with pure Pd) is apparent. The shape of the Si *LVV* structure indicates no significant segregation of Si, and the peak intensity at 312±1 eV was about similar to that in Fig. 1(a). In this stage, formation of epitaxial Pd_2Si was revealed by RHEED. Upon annealing the sample at 350 °C for about an hour, Si segregated strongly to the surface, while the peak height at about 312 eV increased also. The same result was obtained when the deposition of Pd was performed at 350 °C, as is shown in Fig. 2(b). When the segregated Si layer was partly sputtered off by ion bombardment (at room temperature) the splitting of the Si *LVV* peak reappeared, concomitant with a strong decrease of the peak height at 312 eV, as is shown in Fig. 2(c). Moreover, the background below 320 eV was slightly reduced, which indicates that the Si overlayer had contributed to it in the spectrum in Fig. 2(b). Furthermore, the strong decrease of the peak intensity of Si indicates that formation of silicide islands with unreacted Si in between was not significant. From this, the thickness of the segregated Si layer could roughly be estimated to about 0.3 nm, in agreement with findings by other authors.[6] No ordering of this layer could definitely be detected by our RHEED technique, although a superstructure has been seen by other authors by LEED.[6] It may be surprising that in Figs. 2(b) and 2(d) no splitting of the Si *LVV* peak is apparent, although the RHEED patterns clearly showed the existence of Pd_2Si, and a characteristic sign of Pd is seen by the weak peak at 43 eV. However, the Auger electrons emitted from the silicide have to pass through the segregated Si overlayer and suffer strong energy losses, such that the expected splitted structure is smeared out and barely visible on the steep background of the Si peak at 92 eV.

It is worth noting that the RHEED pattern of epitaxial Pd_2Si did not change during further sputtering. Subsequent annealing at 500 °C caused again segregation of Si and an increase of the peak height at 312±1 eV, as well as of the background [see Fig. 2(d)]. Similar results were obtained on clean Si(100), although no epitaxial silicide films could be produced on these substrates.

B. Native oxide-covered substrates

When room-temperature deposits of Pd on native oxide-covered Si substrates are annealed at temperatures above about 200 °C, or when the depositions are carried out at such temperatures, silicide formation occurs by penetration of Pd through the oxide layer into the substrate.[2,3] For deposition or annealing temperatures above 250 °C, our Auger spectra revealed strong segregation of Si, as well as an increased peak height at 312±1 eV. This is shown in Fig. 3(a) for 3.5 nm of Pd deposit-

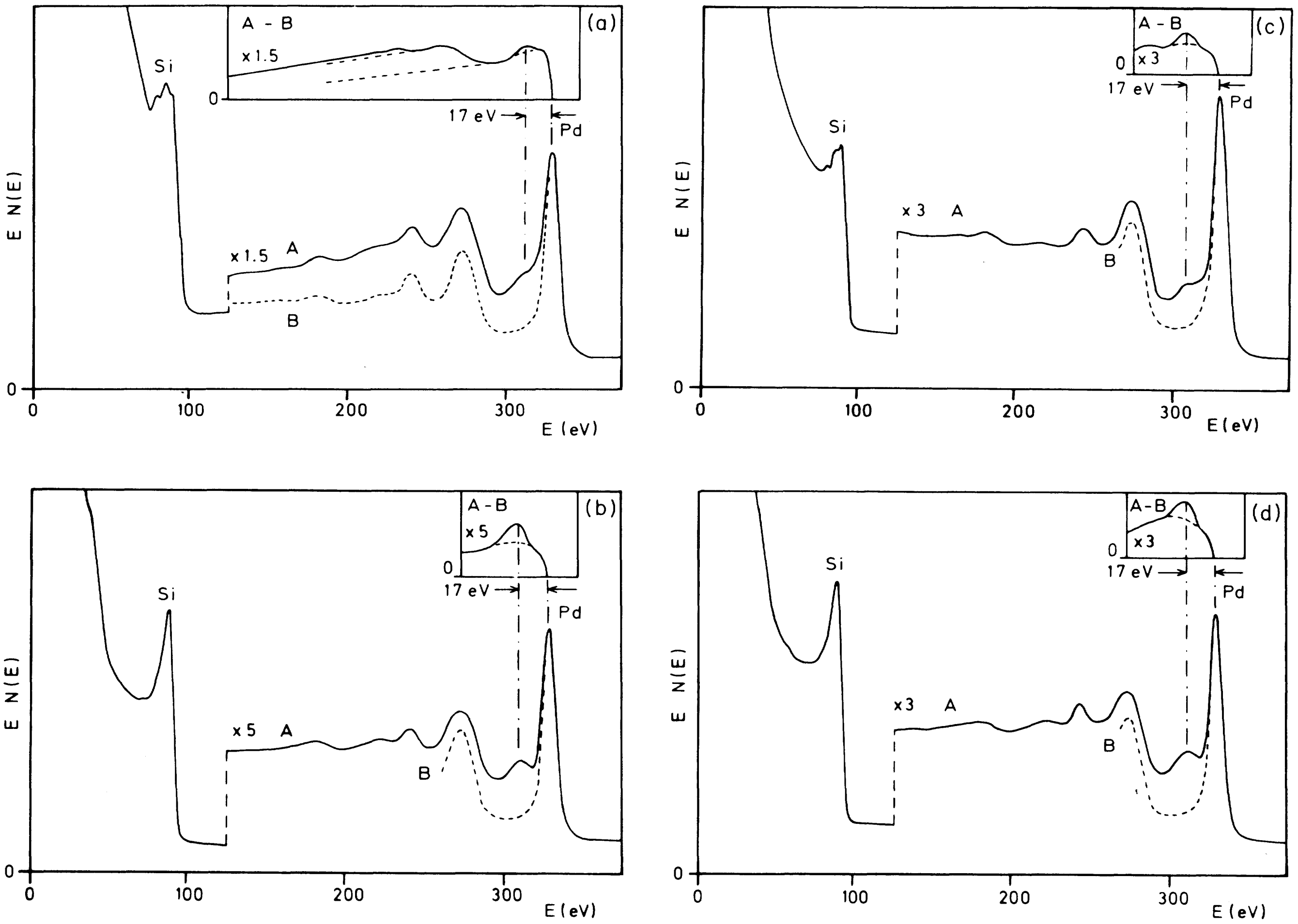

FIG. 2. (a) Spectrum of Pd_2Si (A) formed by deposition of Pd of 3.5 nm equivalent thickness on Si(111) at 230 °C. The dashed curve (B) is a normalized spectrum of Pd. The difference spectrum is shown in the insert, where the estimated contributions of the low-energy tails of the Pd Auger lines to the background, as well as of the additional peak at $\Delta E = 17$ eV, are indicated. (b) Silicide spectrum obtained after deposition of Pd of 3 nm equivalent thickness on Si(111) at 350 °C. Note the enhanced signal of Si at 92 eV, and of the peak at $\Delta E = 17$ eV below the main line of Pd at 330 eV. In the difference spectrum (insert), the estimated background below this peak is indicated. (c) Same sample as in (b) after short Ar-ion sputtering at room temperature. Compare the shape of the silicide structure with that in Fig. 2(a). (d) Same sample after subsequent annealing at 500 °C for 30 min. Si enrichment has reappeared.

ed at 550 °C on Si(111) (ox.). The strong oxygen Auger peak at 507 eV as well as the peak at 76 eV due to oxidized Si, concomitant with a strong signal of pure Si at 92 eV, indicate a rather inhomogeneous lateral distribution of the elements, such that Pd-silicide with segregated Si had locally formed, whereas oxidized Si was present between the silicide islands. In fact, formation of polycrystalline Pd_2Si was revealed by RHEED. When the surface oxide was mostly sputtered off by ion bombardment, the segregated Si layer was removed also while the Pd Auger signal at 330 eV increased strongly. The splitting of the Si *LVV* structure indicated the presence of Pd_2Si at the surface, and the peak intensity at 312 eV decreased sharply. This is shown in Fig. 3(b). The increase of the Pd Auger signal at 330 eV during sputtering was much stronger than in the case of Pd_2Si formed on clean Si substrates, where the segregated Si overlayer had been sputtered off [compare Figs. 2(b) and 2(c)]. This indicates that on oxidized substrates part of the silicide had formed below the oxide layer. When this was removed, the amount of silicide being exposed to the surface of the sample increased.

C. Ion sputter induced effects

Extended ion-beam bombardment of room-temperature deposits of Pd on native oxide-covered substrates, which is for example applied for depth profiling, may lead to an enhanced reaction of Pd with the underlying silicon, even in the presence of a thin native oxide interface. This is illustrated by Auger spectra shown in Figs. 4(a) and 4(b). The Si *LVV* splitting develops during

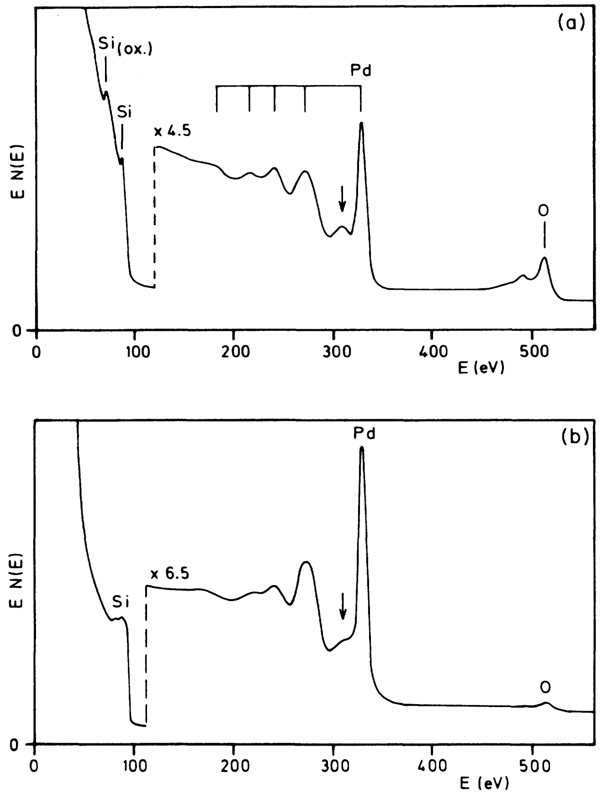

FIG. 3. (a) Silicide spectrum obtained after deposition of Pd of 3.5 nm equivalent thickness on native oxide-covered Si(111) at 550 °C. (b) Same sample, after short Ar-ion sputtering.

sputtering due to ion-induced formation of silicide. The shape of this structure indicates some segregation of Si by a somewhat increased intensity at 92 eV, while a small peak appears at 313±1 eV, and the background is enhanced similar to the examples in the foregoing sections. At this stage, virtually no signal was detected at 76 eV of oxidized Si, although a small oxygen peak was still present at 507 eV. This means that most of the oxide was removed and/or partly dispersed in the silicide. During further sputtering, the Auger peak height of Pd at 330 eV continued to decrease, while the peak of Si at 92 eV increased strongly [see Fig. 4(b)]. Apparently the silicide was broken up such that substrate silicon became exposed at the surface and silicon was enriched on the silicide islands. This is most probably due to preferential sputtering of Pd, as the ratio of the sputter yields of Pd to Si was about 5 for our experimental conditions. The peak at about 313 eV was well developed, similar to the results from deposition and annealing experiments described above. In this stage, no oxygen was detectable any longer.

IV. DISCUSSION

Our systematic studies of the Pd-Si reaction on clean and native oxide covered Si substrates have revealed that Auger spectra always shown an additional, more or less pronounced peak at 312–313 eV, e.g., about 12–13 eV below the main Pd *MVV* line at 330 eV. The intensity of this peak turned out to be especially strong, and the peak width small, when the samples were treated to temperatures above 250 °C, either during deposition of Pd or after the deposition was completed, such that silicon segregated substantially to the surface of the silicide. Sputtering off this Si overlayer caused a strong reduction of the peak intensity.

An estimate of absolute intensity values was obtained in the following way. As is indicated in the spectra, for example in Fig. 2(b), Auger spectra of pure Pd were subtracted from silicide spectra after subtraction of constant background values corresponding to background values at energies above 350 eV in the respective spectra and after normalization to the peak heights at 330 eV. From the difference spectra, a roughly continuous background below the peak at around 313 eV was estimated. This background possibly originates from a superposition of a broad spectrum of energy losses and of a specific loss of about 24 eV in the silicide (see below). The resulting net

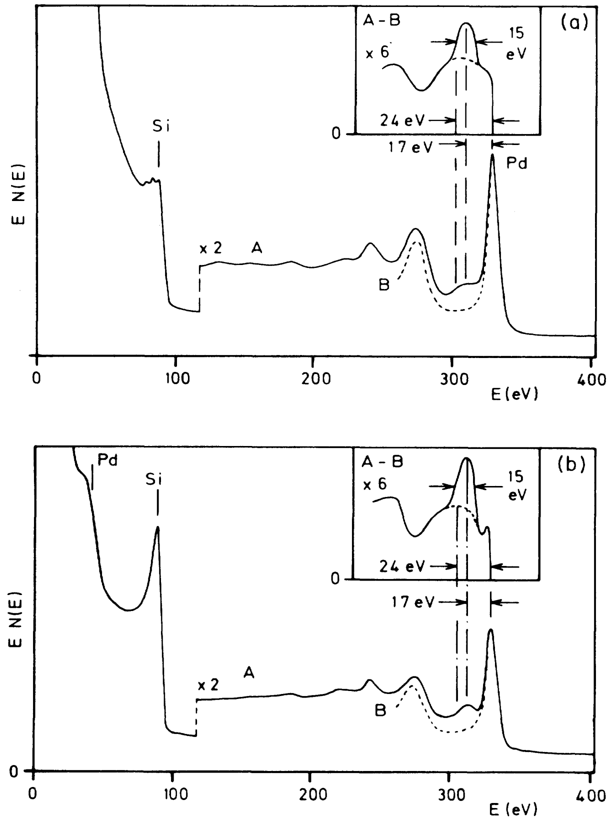

FIG. 4. (a) Silicide spectrum obtained after deposition of Pd of 2.5 nm equivalent thickness on native oxide-covered Si(100) at room temperature, and after subsequent Ar-ion sputtering. The signal-to-background ratio of the oxygen Auger peak at 507 eV was 0.25. The inset shows the difference spectrum with respect to pure Pd. The estimated background below the peak at $\Delta E = 17$ eV exhibits a maximum value at around $\Delta E = 24$ eV. (b) Same sample after prolonged sputtering. Only traces of oxygen were present in this stage.

intensity I_l' of the peak at about 313 eV was then normalized to the Auger peak height I_{Pd} of Pd at 330 eV. In Fig. 5, these data are plotted versus the signal-to-background values of the Si LVV transition I_{Si}/I_b. A clear linear correlation is apparent for the case of originally clean Si substrates (open circles), although the data had been collected from different samples with varying deposition and/or annealing temperatures. This may indicate that the morphology of the silicide was rather similar in each case. Especially, island formation, analogous to what has been reported to occur for ultrathin silicide layers (<1.5 nm) on Si at and above 300 °C,[9] is not thought to be significant here, as was mentioned in Sec. III A. Although islands may have formed in the nucleation stage, these have most probably coalesced at higher coverages. At least, no contrast of islands could be detected by scanning electron microscopy at a resolution of 7 nm. For samples which were originally covered with native oxide, the data were generally higher than for the former cases at the same I_{Si}/I_b ratio (solid circles). The origin for this is not clear at present, but may be due to some dissolution of oxide or oxygen in the silicide,[2,3] by which the Auger peak intensity of Pd would be reduced and the apparent ratio I_l'/I_{Pd} would be increased.

These results suggest that the origin of the peak in question is a plasmon loss of Pd $M_{4,5}VV$ Auger electrons in the segregated Si overlayer. The observed linewidth of 15±1 eV would also correspond to this interpretation. Taking into account the linewidth of the Pd MVV Auger transition of about 10 eV, the linewidth of the loss peak in Si would be of the order of 5 eV, which is close to the literature value of 3.7±0.5 eV for the loss of 17 eV in Si.[10] Whether the remaining, slight broadening is due to the reduction in "dimensionality" of the Si layer of 2–3 monolayers thickness, or is due to some Pd being dissolved in that layer, cannot be judged at present. Possibly, high-resolution energy-loss spectroscopy (ELS) studies may clarify such questions.

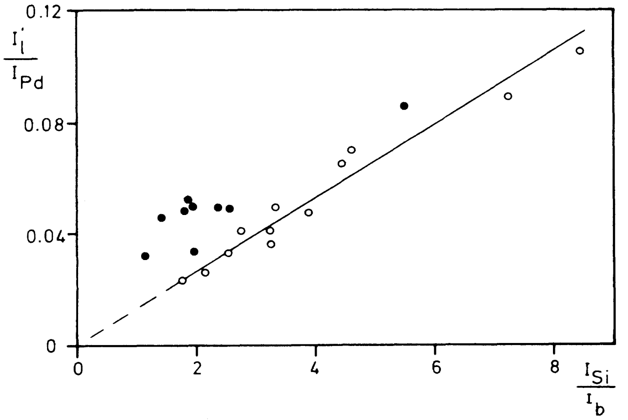

FIG. 5. Plot of the normalized intensities I_l'/I_{Pd} of the peak at $\Delta E=17$ eV vs the signal-to-background ratio I_{Si}/I_b of Si as explained in the text. Open circles: data from originally clean samples; solid circles: data from samples which were originally covered with native oxide. The data were collected from various samples which had been subjected to different Pd deposition and/or annealing temperatures. The amounts of initially deposited Pd ranged from 0.35 to 3.5 nm equivalent thickness.

Finally, the value of the ratio I_l'/I_{Pd}, ranging from 0.02 to 0.11, would be typical for relative loss-peak intensities obtained with low-energy electrons in backscattering mode.

As mentioned above, the background below the loss peak could be partly caused by a plasmon loss in $\mathrm{Pd_2Si}$. In fact, ELS studies have revealed a peak at 24 eV, which was attributed to a plasmon loss in Si, being shifted to higher energies due to the higher electron density in the valence or conduction band of the silicide.[3] Our Auger difference spectra only exhibited a rather broad feature at the corresponding energy of 306 eV. Assuming that the loss of 24 eV contributed to our spectra, the broadening is possibly due to inhomogeneities in stoichiometry, most probably by local variations at the interfaces.[4] Thus, the background feature in our spectra would be a superposition of this loss peak at around 24 eV and of a continuous background of other losses. The escape depth of electrons of energy 330 eV is about 0.8 nm, which would be sufficient for exciting plasmons quasisimultaneously in the silicide and in the segregated Si overlayer.

V. CONCLUSION

Our AES studies of the Pd-silicide reaction on clean and native oxide-covered Si substrates have shown that careful analysis of $N(E)$ spectra revealed several features, which had not been appreciated in earlier work. The occurrence of an additional peak at about 313 eV was correlated to segregation of Si on $\mathrm{Pd_2Si}$, especially for reaction temperatures at above 250 °C. This peak was attributed to a plasmon loss in the Si overlayer, being excited by Pd $M_{4,5}VV$ Auger electrons. Below 250 °C, segregation of Si was much less pronounced, but still a rather broad peak appeared at around 306 eV, which may be partly due to a plasmon loss in $\mathrm{Pd_2Si}$ expected at this energy. This peak appeared to be smeared out, possibly by variations of the stoichiometry at the interfaces, and was superposed on a continuous background of other inelastic losses. This background enhancement was found in the entire range of energies from about 100 to 320 eV, e.g., at the low-energy tails of the major Auger lines of Pd, and was caused by silicide formation.

In the case of substrates, which were originally covered with native oxide, the silicide had grown rather inhomogeneously and the degree of epitaxial orientation was much less than on clean substrates. This will be discussed in another paper. Nevertheless, segregation of Si was found on silicide islands.

Finally, it was shown that ion sputtering induces the silicide reaction, and an enrichment of Si at the surface, even in the case of native oxide interfaces being present and even at room temperature. This has to be taken into account when interpreting ion-sputter depth profiles in the case of such highly reactive systems.

[1] For a recent review, see, for example, Proceedings of the Workshop on Refractory Metal Silicides for VLSI II, San Juan Bautista, California [J. Vac. Sci. Technol. B **2**, 689 (1984)].

[2] D. M. Scott, S. S. Lau, R. L. Pfeffer, R. A. Lux, J. Mikkelson, L. Wielunski, and M.-A. Nicolet, Thin Solid Films **104**, 227 (1983).

[3] R. Anton, Thin Solid Films **118**, 293 (1984); **125**, 305 (1985).

[4] G. W. Rubloff, P. S. Ho, J. F. Freeouf, and J. E. Lewis, Phys. Rev. B **23**, 4183 (1981).

[5] Z. Lilienthal, R. W. Carpenter, and R. Tuenge, Thin Solid Films **104**, 17 (1983).

[6] K. Oura, S. Okada, and T. Hanawa, Appl. Phys. Lett. **35**, 705 (1979); S. Okada, K. Oura, T. Hanawa, and K. Satoh, Surf. Sci. **97**, 88 (1980); K. Oura, S. Okada, Y. Kishikawa, and T. Hanawa, Appl. Phys. Lett. **40**, 138 (1982).

[7] P. S. Ho, G. W. Rubloff, J. E. Lewis, V. L. Moruzzi, and H. R. Williams, Phys. Rev. B **22**, 4784 (1980).

[8] R. Anton, Thin Solid Films **81**, 53 (1981).

[9] R. M. Tromp, E. J. van Loenen, M. Iwami, R. G. Smeenk, F. W. Saris, F. Nava, and G. Ottaviani, Surf. Sci. **128**, 224 (1983).

[10] H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons,* Vol. 88 of *Springer Tracts in Modern Physics* (Springer, Berlin, 1980).