Impurity effects in transition metal silicides

C.-D. Lien and M-A. Nicolet
California Institute of Technology, Pasadena, California 91125

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Impurities can affect the properties of silicides directly by virtue of their presence. Impurities can also influence the processes by which silicides are formed. The effect of impurities on the reaction of transition metal films with a silicon substrate induced by thermal annealing are well documented. The interpretation of these results is discussed. It is shown that impurity redistribution is a major factor in determining how significant the effect of an impurity is. Redistribution observed for dopant impurities is also discussed.

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I. INTRODUCTION

Thin silicide films are important in VLSI as interconnects and contacts.[1-8] However, the reproducibility of a thin silicide film may be affected by the presence of impurities. An impurity may enter the silicide at various stages of processing and be found at various locations. They can affect the properties of a silicide directly by virtue of their presence, e.g., impurities in the silicide film may change the film's resistivity,[9-12] etching properties,[45] stress,[46] adhesion to the substrate,[47] and many other parameters, such as grain size, thermal expansion coefficient, oxidation rate, etc. Impurities can also alter the properties of a silicide indirectly by altering the silicide formation processes, e.g., impurities in the sputtering gas can affect the stoichiometry of the deposited film,[13-15] or they can modify the outcome of the silicide formation by reaction of a metal film with a Si substrate.[16-39] For the purpose of this discussion, we shall define impurity as oxygen, nitrogen, carbon, noble gases, dopants, and other metals of which the atomic concentration is a few percent or less.

A comprehensive investigation of the effect of impurities on every relevant parameter of every silicide of interest for each impurity listed above would be a monumental undertaking. Measured on that scale, the existing information on the subject is minimal and sporadic. In addition, much of the information available is phenomenological, in the sense that it described the changes observed in the resistivity, or some other parameters of a silicide, as a result of impurities present in the system used for the silicide formation. This information is applicable only in combination with a particular setup. We shall, therefore, not dwell much on this type of study. Rather, we concentrate on those instances where the results are independent of a particular system.

To obtain that type of data and approach the topic in a systematic way, the questions that have to be addressed are: (i) What is the chemical identity of the impurity in the sample? (ii) How much of it is there? (iii) Where is it? Only with these three facts on hand does it become possible to understand the effects of impurities in basic terms. The bulk of this review discusses experiments where answers to all three questions are available. Experiments of this kind are typically executed in such a way that the nature of the impurity and its concentration are initially known. The main issue then concerns initial location and redistribution of the impurity. As will be seen, an understanding of the effects of impurities often requires that information as an essential input.

Table I categorizes the redistribution of impurities when present in the bulk of the film or the substrate. The entries in the table identify the main mechanisms that are responsible for the redistribution of the impurity. Two limiting behaviors of the impurity are conceivable, depending on whether the impurity is mobile or not by annealing at a temperature for a fixed time (e.g., oxygen in Ni at 300 °C for 2 h is immobile and nitrogen in Ni at 300 °C for 30 min is mobile. Note that it is possible that the same impurity in the same sample can belong to the immobile case at low temperatures and to the mobile case at high temperatures). Only two kinds of

TABLE I. Several categories of bulk impurity redistributions in media with different impurity diffusion rates during annealing. Entries in the table identify the main mechanisms for the impurity redistribution.

			Impurity redistributions: Immobile	Impurity redistributions: Mobile	Application
Medium	Stable silicide film on Si		I None	II Diffusion	Interconnects
	Reacting silicide or metal film on Si	No diffusion enhancement	III Kinetics of silicide formation	V Diffusion + kinetics of silicide formation	Contacts
		Diffusion enhancement	IV Kinetics of silicide formation		

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media are considered: one is typical for the application of silicides for interconnects, and the other for contacts. As an interconnect, the structure of interest is a stable silicide film on top of a poly-Si film. The parameter of primary concern is the sheet resistence. Here the main questions are how the impurity redistributes upon thermal annealing and how this alters the sheet resistance. The prototype of this case is listed in Table I as a stable silicide film on Si (category I and II). For the immobile diffusing impurities (category I) there is no redistribution of the impurity during annealing. The effect of an impurity in the silicide in this case is due simply to the presence of the impurity.[9–12] For the mobile impurities (category II) the diffusion induced by thermodynamic driving forces determines the redistribution.[40–45] In that case, the effect of the impurity depends both on its amount and its distribution. For the Ohmic or Schottky barrier contacts, the typical initial structure is the elemental metal layer subsequently reacting with the single crystalline Si substrate to form a silicide–silicon contact. The primary parameters of interest are the barrier height for a Schottky contact and the contact resistance for an Ohmic contact. The main questions here are how the impurity redistributes upon silicide formation and how this alters the barrier height and contact resistance. The prototype of this case is listed at Table I as a reacting film on Si. For the case of an immobile impurity, its redistribution is mostly determined by the kinetic processes of the silicide formation. We distinguish two cases where the diffusion of the impurity is enhanced by the silicide formation (category IV) and where it is not (category III). For mobile impurities (category V) the redistribution is determined by both the diffusion of the impurity and the kinetic processes of silicide formation.[16–39,48–68] In all these cases, the question is how the properties of the resulting contact and its formation process are affected by the impurity.

For contacts, in addition to bulk impurities, the interfacial impurities (e.g., native or intentionally introduced impurity on Si) are also important because these interfacial impurities can have a major effect on the electrical properties of a contact by virtue of their presence,[74] or by altering the contact structure. Here, we will define the interfacial impurity layer as thin, thick, or nonuniform functionally by its effect on the silicide formation. In the thin interfacial impurity layer, the silicide reaction proceed laterally uniformly; for the thick interfacial impurity layer, the silicide formation is stopped completely. A nonuniform interfacial impurity layer is one which is thin in some places and thick in others. The redistribution of the interfacial impurity and its effect are similar to the category III in Table I.

II. SAMPLE PREPARATION AND ANALYSIS

Generally, the samples are prepared by depositing thin films on a chemically cleaned substrate (or a substrate with intentionally introduced impurity) either by electron gun or by sputtering in a well-controlled atmosphere or, more recently, by chemical vapor deposition (CVD). In most cases, the substrates are silicon wafers and the films are thin metal (Si–M), or amorphous silicide (Si–a-silicide), or crystalline

TABLE II. The redistribution and effect of impurities in the sample with structure: Si substrate (or poly-Si film)—stable silicide film. All samples were annealed, except a-$CrSi_2$.

Silicide	Impurity	Location of impurity		Resistivity	Conservation of impurity	Refs.	Category (Table I)
		as-prepared	annealed				
a-$CrSi_2$[a]	O_2[b]	$CrSi_2$		increases		9	I?
$TiSi_2$[a]	N_2[b]	$TiSi_2$	$TiSi_2$	increases			I?
	P	poly-Si		increases	loss	42	II
	As[c]	poly-Si	$TiSi_2$	increases		42	II
	Sb[c]	$TiSi_2$	poly-Si	decreases		42	II
$MoSi_2$[a]	P[c]	$MoSi_2$	$MoSi_2$	increases		10	II
	P[b]	$MoSi_2$	$MoSi_2$[i]			11	II
$MoSi_2$[d]	O_2[e]	$MoSi_2$		same		12	I?
	N_2[e]	$MoSi_2$		same		12	I?
	H_2O[e]	$MoSi_2$		increases		12	I?
Mo_3Si[d]	O_2[e]	Mo_3Si		same		12	I?
	N_2[e]	Mo_3Si		same		12	I?
	H_2O[e]	Mo_3Si		increases		12	I?
$TaSi_2$[a]	O[b]	$TaSi_2$		increases		2	I?
	P[c]	poly-Si	$TaSi_2$ + poly-Si	increases	loss[g]	40,41	II
WSi_2[d]	As[c]	poly-Si	poly-Si[f]		loss[g]	43,44	II
	P[c]	poly-Si	poly-Si[f]		loss[g]	43.44	II
	P[h]	poly-Si	poly-Si[f]		loss[g]	45	II
	B[c]	poly-Si	WSi_2[f]		loses a little[g]	43,44	II

[a] Cosputtered silicide.
[b] Impurity introduced in the sputtering gas.
[c] Implanted impurity.
[d] Coevaporated silicide.
[e] Impurity introduced in the evaporation system.
[f] Film with higher solid solubility of impurity than the other film.
[g] Loss of dopant can be suppressed by using a CVD silicon oxide cap.
[h] Impurity introduced during CVD process.
[i] If capped with SiO_2, P will diffuse into Si substrate.

silicide (Si–silicide). To study the impurity effect in properties of a silicide, controlled amounts of impurities need to be introduced into some of the samples either during preparation or during processing. In the first case, impurities can be introduced by adding gaseous impurities in the evaporation,[12] or sputtering, or CVD system, or by implanting impurities into the bulk of the thin film or Si substrate,[16] or by slightly oxidizing the Si substrate surface.[77] Most of the samples with and without impurities are then annealed in a furnace with a controlled ambient. In the second case, samples are annealed with controlled impurities introduced in the annealing system.[70,71] Samples are then measured after annealing. The experimental techniques used most to study the properties of silicides and the distribution of impurities are Rutherford backscattering spectrometry (RBS), nuclear reactions (NRA), x-ray diffraction, secondary ion mass spectrometry (SIMS), Auger electron spectrometry (AES), transmission electron microscopy (TEM), optical microscopy, four-point probe, I–V, and C–V measurements.

III. REDISTRIBUTION AND EFFECT OF IMPURITIES IN STABLE SILICIDE

The immobile impurities (category I of Table I) will not redistribute during annealing and, therefore, affect the properties of a silicide only by their presence in atomic or compound form (see Table II, resistivity entry). One of the examples listed in Table II is given in Fig. 1 which shows the effect of nitrogen in sputtered $TiSi_2$ film on film resistivity. The impurity (N_2) was added to the sputtering gas (10 mTorr Ar) to introduce the impurity in the sputtered film ($TiSi_2$). The films were then annealed in vacuum at a residual pressure $< 10^{-6}$ Torr. The as-deposited films which are amorphous as identified by x-ray diffraction have high sheet resistance. After annealing the $TiSi_2$ crystallizes and the sheet resistance of the film goes down for samples with or without nitrogen contamination. Also as indicated in Fig. 1, the sheet resistance of as deposited as well as the annealed film increases as the content of nitrogen increases.

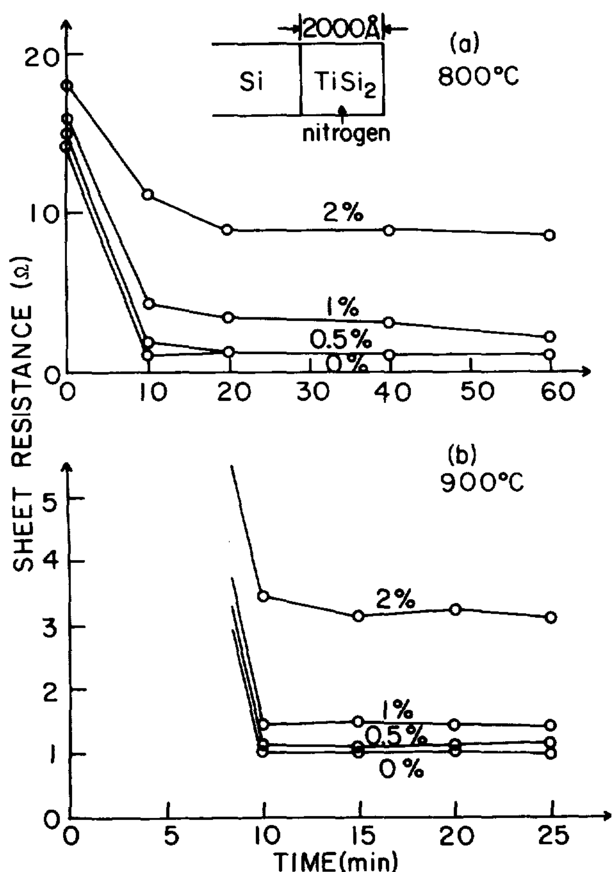

FIG. 1. Sheet resistance of $TiSi_2$ films which contain about 5, 7.5, 10, and 15 at.% of N (formed by adding 0, 0.5, 1, and 2% of N_2 to the 10 mTorr sputtering Ar gas) are plotted against annealing time. $TiSi_2$ film (about 2000 Å) was deposited on a Si substrate of resistivity about 5–30 Ω cm and annealed without a cap in vacuum with pressure $< 1 \times 10^{-6}$ Torr at (a) 800 and (b) 900 °C.

For the case of mobile impurities (category II in Table I) the impurity (in general a dopant) redistributes during annealing according to the diffusivities, and subjects to the constraint of solid solubilities of each layer (in general, the samples configuration is a SiO_2 substrate–poly-Si film–refractory silicide film). Sometimes there is a dielectric cap (e.g., SiO_2) deposited on the top of the sample to avoid the evaporation of dopant into the ambient during annealing (see Table II). The redistribution of impurity can affect the resistivity and etching properties of interconnection lines and threshold voltage of MOS devices.[14] Figure 2 shows the redistribution of implanted dopants (a) B, and (b) As in the samples: SiO_2 substrate–poly-Si–WSi_2–poly-Si after annealed at 1000 °C in N_2. The dopant profiles in samples of (1) as-implanted, (2) annealed for 2 h, and (3) annealed for 27 h

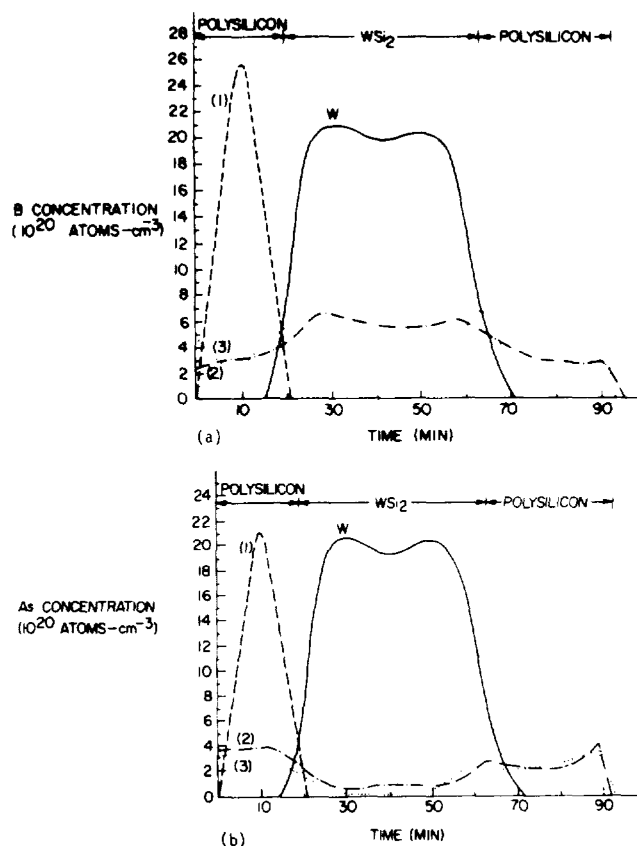

FIG. 2. Dopants (a) B and (b) As profiles as a function of sputtering time for (1) as-deposited samples, (2) samples annealed at 1000 °C in N_2 for 2 h, and (3) samples annealed at 1000 °C in N_2 for 27 h (see Ref. 44).

TABLE III. The redistribution and effect of impurities in the sample with structure: reacting film on Si (nonrefractory metal silicides).

Silicide	Impurity	Location of impurity as-prepared	Annealed	Growth rate	Conservation of impurity	Refs.	Category (Table I)
Ni_2Si	^{16}O	Ni	Ni_2Si/Ni	slow	gain	16–18,48	III
	O	ambient	Ni_2Si/Ni	slow	gain	69	
	^{16}O	Si	Ni_2Si	slow	yes	18	III
	Au	Ni	Ni_2Si/Ni	slow[a]		19	III
	^{14}N	Ni	Ni_2Si/Ni	slow		20,21,50	V
	^{15}N	Ni	Ni_2Si/Ni		loss	49	V
	^{15}N	Si	Ni_2Si		yes	49	III
	As	Si	$Ni_2Si/Ni,Ni_2Si$			54	IV
NiSi	^{16}O	Ni_2Si	NiSi	slow		22	III
	Sb	Si	NiSi			51	III?
	As	Si	Si/NiSi,NiSi			54	IV
$NiSi_2$	Xe	NiSi	$NiSi_2$	slow	yes	23	III
	^{18}O	NiSi	$NiSi_2$	slow	yes	23	III
Co_2Si	^{18}O	Co	Co_2Si/Co	same	yes	24	III
	^{18}O	Si	Co_2Si	fast	yes	24	III
	^{15}N	Co	Co_2Si/Co	slow	loss	57	V
	^{15}N	Si	Si/CoSi	fast	yes	57	III
CoSi	^{18}O	Si	Si/CoSi	slow	yes	24	III
	^{15}N	Si	Si/CoSi	slow	yes	57	III
Pd_2Si	^{16}O	Pd	Pd_2Si	same	gain	16	III or V
	^{18}O	Pd	$Pd_2Si,Pd_2Si/Pd$	same	loss	56	III or V
	^{18}O	Si	Si/Pd_2Si	slow	yes	56	III
	^{15}N	Pd	$Pd_2Si,Pd_2Si/Pd$	same	loss	56	III or V
	^{15}N	Si	Si/Pd_2Si	slow	yes	56	III
	O,N,C	Pd		slow		25	III or V
	O,N,C	Si		slow		25	III
	As	Si	$Si/Pd_2Si,Pd_2Si$	slow		26–28,51–54	IV
	P	Si	$Si/Pd_2Si/Pd_2Si$			55	IV
	Sb	Si	Pd_2Si			51	
Pt_2Si	O	Pt		slow		16,29,30	III
	Rh	Pt		slow		32	III?
	O,Al	Pt	Pt_2Si/Pt			59,60	III
	^{18}O	Pt	Pt_2Si/Pt		yes	58	III
	^{15}N	Pt	Pt_2Si/Pt		yes	49	III
	^{15}N	Si	Pt_2Si		yes	49	III
	As	Si	$Pt_2Si/Pt,Pt_2Si$	slow		31,53,54	IV
PtSi	O	Pt		slow		29	III
	O	ambient	PtSi/Pt	slow	gain	70–73	
	As	Si	Si/PtSi,PtSi	slow		31,61–64,53,54	IV
	P or Sb	Si	Si/PtSi,PtSi			53,54,66	IV
	B or In	Si	PtSi			64,65	

[a] Annealed at temperatures less than the Au–Si eutectic (i.e., 370 °C).

are shown in this figure.[44] This shows that the solid solubility of B is higher in WSi_2 than in the poly-Si layer. But the solid solubility of As is higher in the poly-Si than in the WSi_2 layer.

IV. REDISTRIBUTION AND EFFECT OF IMPURITIES IN REACTING SILICIDE OR METAL FILM ON Si

The redistribution and the effect of impurities in samples whose initial structures consist of a reacting film on a Si substrate are listed in Table III (nonrefractory metal silicides) and Table IV (refractory silicides). Again, we classify the bulk impurities into immobile (categories III and IV) and mobile (category V) impurities during annealing, as defined in Table I. The immobile case is subdivided into groups with (category III) or without (category IV) enhanced impurity redistribution. For the mobile impurities, we cannot in general distinguish between a redistribution process with or without enhancement; therefore, only one category (V) is used here.

Scott[16] has proposed a model to explain the redistribution and the effect of oxygen and nitrogen (category III) in silicide formation in terms of two parameters, namely, the moving species during silicide formation and the reactivity of the impurity with the metal and the Si. The model is generalized by the author of this paper for all the immobile impurities (category III) and uses only the moving species parameter to explain the redistribution and the effect of impurities. The modified model (see Fig. 3) assumes that there is a dominant moving species during the silicide formation [say metal (M)] and a stationary species (say Si) (i.e., M atoms dissociate at silicide/M interface, migrate through the silicide and form a silicide with Si atoms at the Si/silicide interface). If the immobile impurity (I) is initially present in the stationary spe-

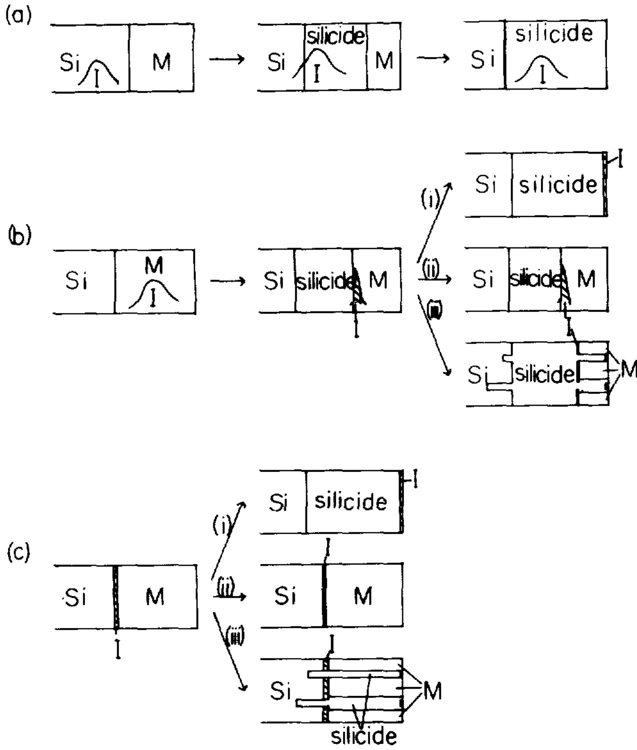

FIG. 3. Model is proposed to explain the redistribution of the immobile impurity during silicide formation. The impurity is initially located either (a) in the stationary species layer, or (b) in the moving species layer, or (c) at the Si/metal interface. In all cases, the metal (M) is assumed to be the moving species and Si to be the stationary species. Corresponding cases exist when Si is the moving species.

cies layer [see Fig. 3(a)], then the impurity will stay stationary with respect to the stationary species during silicide formation due to its immobility. Therefore, the impurity will be uniformly diluted and incorporated in the silicide. In this case impurities may slow down the growth rate of silicide, but the effect is generally small. Figure 4(a) shows an example of this type: ^{18}O (2×10^{16} O/cm^2) was implanted into the Cr film (note that in the Si–Cr sample, the metal is the stationary species and Si is the moving species) of a Si–Cr sample as an impurity (I).[33] Samples were then annealed at 450 °C in vacuum. The silicide formed is $CrSi_2$ in both implanted and unimplanted samples. However, as shown in the figure the growth rate of silicide in the implanted sample is a little slower than that in the unimplanted sample. Also the oxygen is incorporated in the silicide after $CrSi_2$ formation[33] (not shown here) as modeled in Fig. 3(a).

If the impurity is initially present in the layer of the moving species [see Fig. 3(b), which assumes that metal is the moving species] then as the metal atoms leave the silicide/M interface and migrate through the silicide, the impurity is left behind and accumulates at the silicide/M interface during silicide formation. Therefore, either: (i) the impurity is ultimately accumulated at the silicide surface (similar to the thin interfacial impurity, see next section), or (ii) the impurity that accumulates at the silicide/metal interface interferes with the reaction so much that the silicide formation is stopped uniformly with an unreacted metal film remaining (similar to the case of thick interfacial barrier, see next section). A

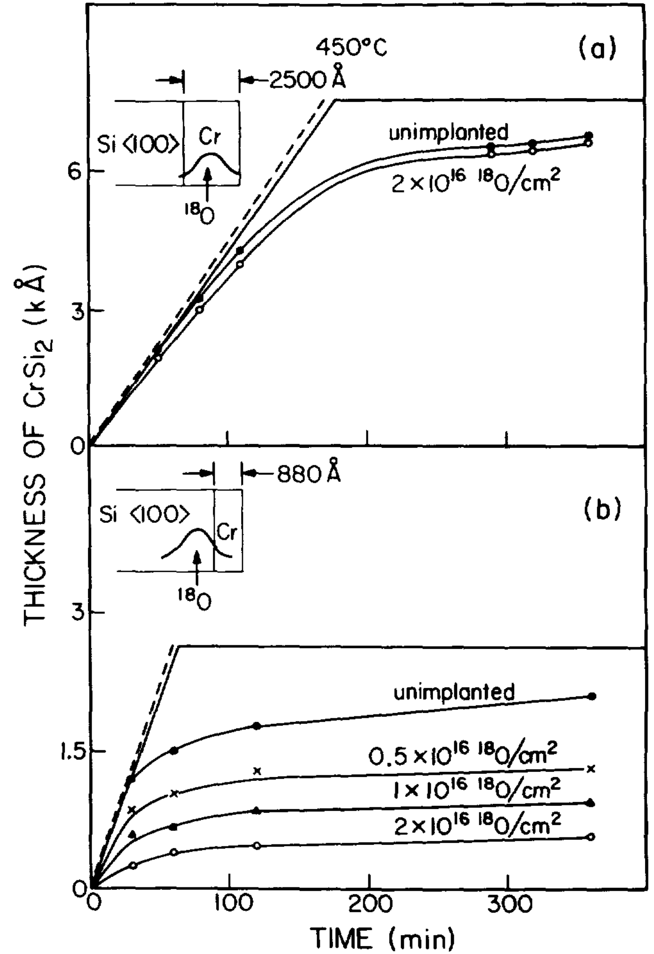

FIG. 4. Growth of $CrSi_2$ at 450 °C: Solid circles are data points for the unimplanted sample; crosses, triangles, and open circles are data points of samples implanted with 0.5, 1, 2×10^{16} $^{18}O/cm^2$, respectively. The peak concentration of the oxygen profile is located either in (a) the Cr film or in (b) the Si substrate. Solid lines and dashed lines represent ideal growth of $CrSi_2$ whose growth rate equals to the initial growth rate of a unimplanted sample measured in Ref. 33 and Ref. 34, respectively (see Ref. 33).

parallel combination of these two cases [see Fig. 3(b) case (iii)] can lead to laterally nonuniform layers (similar to the nonuniform interfacial impurity case, see next section). An immobile impurity initially present in the moving species layer, therefore, has more of an effect on silicide growth than when it is initially located in the stationary species layer. Figure 4(b) shows the growth of $CrSi_2$ with ^{18}O initially implanted into the Si (remember that Si is the moving species) substrate and then annealed at 450 °C.[33] In either implanted or unimplanted sample the phase formed is still $CrSi_2$. However, the growth of $CrSi_2$ was strongly retarded in the implanted sample. The implanted oxygen was piled up at the Si/$CrSi_2$ interface[33] as stated in Fig. 3(b) case (ii). Aside from the growth rate the properties of contact can also be greatly altered when the impurity is initially present in the moving species layer. For the case of the nonuniform silicide formation [see Fig. 3(b) case (iii)] the barrier height value of the contact can be very scattered.[75] Also if, instead of metal, Si is the moving species and contains the impurity, the cases analogous to (i) and (ii) will result in an accumulation of the impurity at the Si/silicide interface. The properties of this Si/

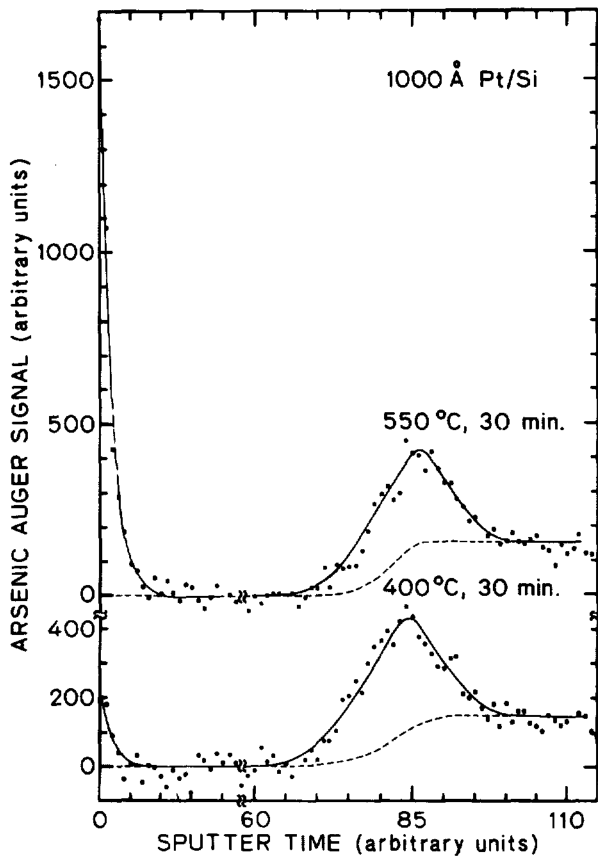

FIG. 5. Auger sputter profile of arsenic (solid line) in a Si substrate (1000 Å Pt film) sample annealed at 400 or 550 °C for 30 min. Dashed lines correspond to the expected As profile if pileup were absent (see Ref. 61).

silicide contact will most certainly be changed by the presence of this impurity. An impurity initially present in the moving species layer, therefore, has a larger effect on the electrical properties of the Si/silicide contact when Si moves than when metal moves.

Many researchers (see Table III) have investigated the redistribution of dopants (mainly As and P) in Si during near noble metal (Ni, Pd, and Pt) silicide formation (annealing temperatures are about 300 °C). They found that although the dopant has very low diffusivity at these low annealing temperatures, part of the dopant is accumulated at the Si/silicide interface and another part incorporated in the silicide during silicide formation (category IV). This phenomenon cannot be explained by the previous model. Wittmer *et al.*[54] proposed another model to explain their results. This model says that a large number of point defects are generated in the Si neighboring the Si/silicide interface during the formation of these silicides and these defects enhance the diffusivity of substitutional dopants at low temperatures. Wittmer *et al.* also reported this snowplow of dopant can reduce the contact resistance for Ohmic contact and possibly be used to adjust the barrier height for Schottky diode.[52] Figure 5 shows the redistribution of the profile of As initially in Si after PtSi formation (by annealed at 400 and 550 °C).[61] The solid line shows the measured profile of As and the dashed lines show the expected profile if pileup were absent.

It is clear that As appeared on the surface of PtSi and at the Si/PtSi interface. The surface part is consistent with the model of Fig. 3, while the interface part needs to be explained by another model (e.g., the model proposed by Wittmer).

In addition to the immobile impurities there are some impurities which diffuse during silicide formation (category V: e.g., N in Ni or Co films, some dopants in refractory silicides, and N or O in refractory metal). The impurity redistribution is either due to its diffusion (e.g., part of the N atoms in the Ni film diffuses to the Si/Ni interface and possibly forms silicon nitride there, while another part moves to the sample surface and evaporates into the surrounding[20,21,49]) or due to both its diffusion and the kinetic processes of silicide formation (e.g., dopant atoms in Si substrate during refractory silicide formation: the dopant atoms stay fixed in Si until the Si/silicide interface reaches their positions, then the dopants will redistribute according to the formation processes of silicide and thermodynamic driving force[35,54]). Examples of redistribution of ^{15}N and ^{18}O in Ta (note that Ta is the stationary species) during $TaSi_2$ formation are given in Fig. 6(a)–6(d), respectively. Figures 6(a) and 6(b) shows the redistribution of ^{15}N initially implanted into Ta during $TaSi_2$ formation by annealing at 675 °C. It shows that most of the implanted N is pushed into the reacted Ta film during reaction.[39] Similar results for implanted ^{18}O are shown in Fig. 6(c) and 6(d). In both cases, the growth of $TaSi_2$ is retarded by the implanted impurities. The result that both nitrogen and oxygen segregate into the Ta film during $TaSi_2$ formation cannot be explained by the model presented in Fig. 3 (remember that Si is the moving species). This result, however, is consistent to that both nitrogen and oxygen have high mobility in Ta and that both have higher solubility in Ta than in $TaSi_2$.

V. INTERFACIAL IMPURITY EFFECT ON REACTING SILICIDE OR METAL FILM ON Si

Interfacial impurities can drastically affect the stability of a contact. Immobile impurities present at the Si/M interface can be characterized as thin, thick, or nonuniform interfacial barriers defined as follows [see Fig. 3(c)]:

(i) Thin barrier: The interfacial impurity is not able to stop the uniform silicide formation and is, therefore, pushed to the silicide/moving species layer interface {see Fig. 3[c(i)] and compare this with Fig. 3[b(i)]}.

(ii) Thick barrier: The impurity stops the silicide formation completely {see Fig. 3[c(ii)] and compare this with Fig. 3[b(ii)]}.

(iii) Nonuniform barrier: The barrier is thin in some places and thick in others. From the above definition, the silicide forms only at the thin part of barrier {see Fig. 3[c(iii)] and compare this with Fig. 3[b(iii)]}.

Note that the definition for an interfacial barrier depends on the sample (i.e., the same interfacial oxide can be thin for some silicides and thick for others), the annealing temperature (e.g., a barrier with is thick at low temperature can be thin at high temperature) and so on. In the case of a nonuniform barrier, the silicide formed has a rough Si/silicide inter-

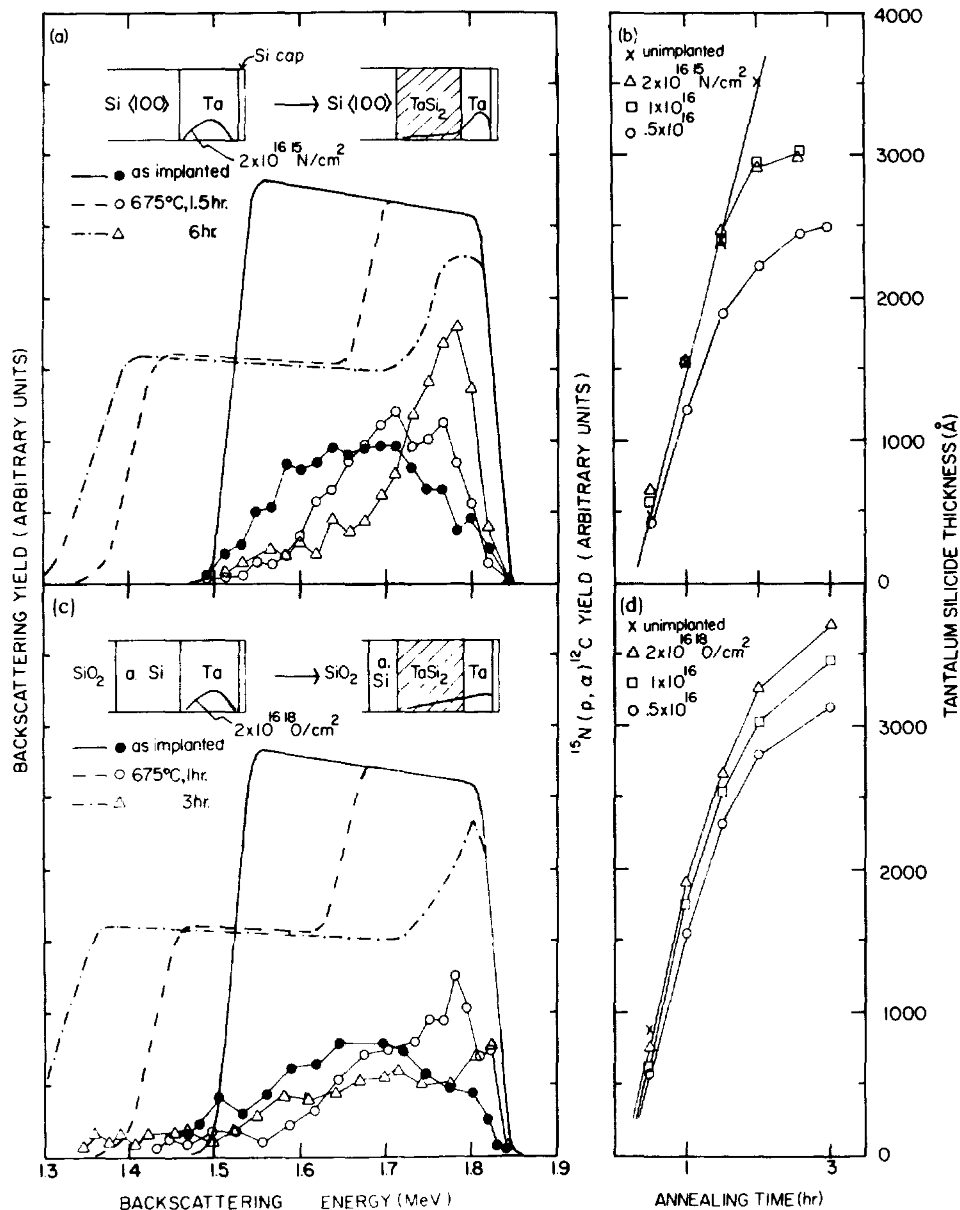

FIG. 6. (a) RBS and NRA spectra of a Si–Ta sample implanted with 2×10^{16} $^{15}N/cm^2$ into Ta and annealed at 675 °C. It shows a pileup of ^{15}N in the unreacted Ta film during reaction. (b) Kinetics curves indicate that implanted N retards the $TaSi_2$ growth (see Ref. 39). (c) RBS and NRA spectra of a Si–Ta implanted with 2×10^{16} $^{18}O/cm^2$ into Ta and annealed at 675 °C. It shows that ^{18}O segregates out of the advancing silicide layer and part of it outdiffuses through the Ta surface. (d) Kinetics curves indicate that implanted O retards the $TaSi_2$ growth (see Ref. 39).

face and a nonuniform surface morphology. The barrier height or contact resistance of a contact, therefore, can be changed drastically. The effect and redistribution of an interfacial impurity are listed in Table V. Examples of thin, thick, and nonuniform interfacial oxides are given in Fig. 7 in which a Pt film was evaporated on a ^{18}O plasma-oxidized Si substrate.[79] Silicon was then implanted through the interfacial oxide. Implanted and unimplanted samples were annealed at 400 °C for 1 h. RBS spectra show that an unimplanted sample does not react at all [i.e., thick barrier, case (ii)]; after a low dose (2.5×10^{15} Si/cm^2 or less) implantation, a nonuniform silicide forms [i.e., nonuniform barrier, case (iii)]; after a high dose (5×10^{15} Si/cm^2) implantation, the silicide forms very uniformly [i.e., thin barrier, case (i)]. The profiles of ^{18}O measured with $^{18}O(p,\alpha)^{15}N$ nuclear reaction show that the locations of ^{18}O are consistent with the predictions of the model shown in Fig. 3(c): the ^{18}O profile in the high dose implanted sample is very narrow and locates at the silicide/moving species interface (full circles); the ^{18}O profile in the low dose implanted sample is broad and located in the silicide (triangles); for the unimplanted sample, the ^{18}O stays at the Si/metal interface and the silicide reaction is stopped (open circles).

VI. SUMMARY

As listed in Table I the redistribution and effect of bulk impurities are classified as five categories:

Category I: There is no redistribution of the impurity during annealing in this case; therefore, the effect of the impurity in a silicide is due to the presence of the impurity.

Category II: The redistribution of the impurity during annealing is due to the impurity diffusion induced by thermodynamic driving force. The effect in silicide properties is due to both the presence and the redistribution of the impurity.

TABLE IV. The redistribution and effect of impurities in the sample with structure: reacting film on Si (refractory metal silicides).

Silicide	Impurity	Location of impurity as-prepared	Annealed	Growth rate	Conservation of impurity	Refs.	Category (Table I)
$CrSi_2$	^{18}O	Cr	$CrSi_2$	slows a little	gain	33	III
	^{18}O	Si	Cr + $Si/CrSi_2$	slows	yes	33	III
TiSi	As	Si	TiSi			53,54	V?
$TiSi_2$	O	Ti	Ti			67	V
	As	Si	$TiSi_2$	slows		35,54	V?
	Sb	Si	$Si/TiSi_2, TiSi_2/Ti$	slows		35	V?
	P	Si		slows		35	
V_3Si	O	V	V			36	V
VSi_2	O	V	V			36	V
	As	Si	VSi_2			53,54	V?
$MoSi_2$	O	Si		slows		37	III?
	O	Mo	Mo/a-si			68	V
	^{15}N	Mo	$MoSi_2$,Mo	slows		38	V
$TaSi_2$	^{18}O	Ta	Ta + $TaSi_2$	slows	loss	39	V
	^{18}O	Si	Si + $Si/TaSi_2$	slows	yes	39	III
	^{15}N	Ta	Ta + $TaSi_2$	slows	loss	39	V
	^{15}N	Si	Si + $Si/TaSi_2$	slows	yes	39	III
	As	Si	$TaSi_2$			53,54	V

TABLE V. The redistribution and effect of interfacial impurities in the sample with structure: reacting film on Si.

Metal	Impurity	Temperature annealed (°C)	Rough interface	Silicide formation	Location of impurity	Refs.
Ni	O^{a}	250 (20 min)		stopped		77
	O^{i}	400 (1 h)		stopped		79
	O^{j}	400 (1 h)	yes	Ni + NiSi	Ni + NiSi	79
	O^{k}	400 (1 h)	no	NiSi	surface	79
Pd	O^{b}	400 (1 h)	yes	Pd_2Si	Pd_2Si	78
	O^{i}	400 (1 h)		stopped		79
	O^{j}	400 (1 h)	yes	Pd_2Si	Pd_2Si	79
	O^{k}	400 (1 h)	no	Pd_2Si	Si/Pd_2Si	79
	O^{h}			Pd_2Si		82
Pt	O^{b}	400 (1 h)	yes	Pt + PtSi		78
	O^{a}	250 (20 min)		stopped		80
	O^{c}	400 (1 h)		Pt + Pt-silicide		83
	O^{d}	400 (1 h)		stopped		83
	O^{i}	400 (1 h)		stopped		79
	O^{j}	400 (1 h)	yes	Pt + PtSi	Pt + PtSi	79
	O^{k}	400 (1 h)	no	PtSi	surface	79
	N^{e}	> 500	yes	Pt + PtSi		81
Cr	O^{a}	450 (45 min)	yes			80
	O^{h}	< 600		stopped		82
Ti	O^{f}	400–600		$TiSi_x + TiO_x$		84
	O^{f}	700–900		$SiO_2 + TiSi_x + TiO_x$		84
	O^{h}			no effect		82
Mo	O^{c}	< 800		stopped		86
	O^{c}	1000		Mo_3Si		86
	O^{g}	950		$MoSi_2$		87
	O^{h}			stopped		82
Ta	O^{g}	950		$TaSi_2$		87
W	O^{g}	< 1050		stopped		87
Er	O^{c}	450	yes	$ErSi_2$		88,89

[a] Si oxidized in solution: $NH_4OH:H_2O_2:H_2O$ = 1:1:5.
[b] Si oxide (about 30 Å) formed in solution: $NH_4OH:H_2O_2:H_2O$ = 1:2:7.
[c] Native Si oxide.
[d] Si oxide (about 30 Å) formed in dry oxygen at 700 °C.
[e] Si sputtered etch with 6 mTorr nitrogen.
[f] Si oxide (< 20 Å).
[g] Dry thermal Si oxide (about 20 Å).
[h] Oxide formed by placing Si in boiling H_2O_2 for 10 min.
[i] *J, k*: Si oxidized in ^{18}O plasma. *i, j*, and *k* are samples implanted by 0, few, and 5×10^{15} Si/cm^2 after metal deposition.

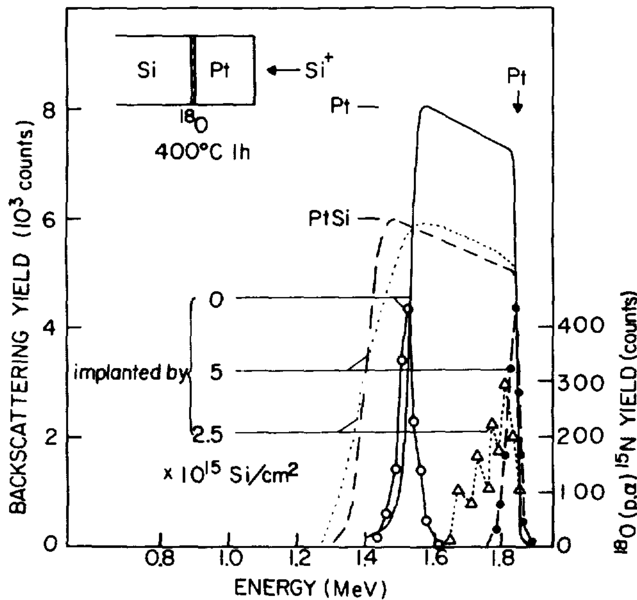

FIG. 7. 2 MeV RBS spectra (Pt signal only) of Si–Pt samples annealed at 400 °C for 1 h. The solid line shows the spectrum of the unimplanted sample. Dotted lines and dashed lines show the spectra of 2.5 and 5×10^{15} Si/cm^2 implanted samples, respectively. The ^{18}O signals of the unimplanted sample (open circles), the low dose implanted sample (triangles), and the high dose implanted sample (full circles) are also shown here. The horizontal scale of ^{18}O signal is adjusted so that the ^{18}O and Pt have the same physical position in the sample when their signals have the same horizontal position in the figure (see Ref. 79).

Category III: The redistribution of the impurity during annealing can be explained by a modified model which was originally proposed by Scott[16] (see Fig. 3). An immobile impurity initially present in the moving species layer has more of an effect on the growth rate of a silicide than it is initially located in the stationary layer. In the former case the silicide formed can be nonuniform which will change the contact properties a lot.

Category IV: The redistribution of the dopant (initially located in Si) during near-noble silicide formation is enhanced by defects induced by silicide formation as proposed by Wittmer *et al.*[54] (snowplow effect). This can greatly alter the properties of silicide Si contacts.

Category V: The redistribution of the impurity which is mobile either due to its diffusion (e.g., N in Ni or Co) or due to both the diffusion and kinetic processes of silicide formation (e.g., dopants redistribution during refractory silicide formation). The effect of the impurity is due to the presence and redistribution of the impurity.

The interfacial impurity (considering immobile case only) can also have a big effect on the silicide formation. Its redistribution and effect on the silicide formation is similar to the bulk impurity category III with the impurity in the moving species layer initially.

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[1]M-A. Nicolet and S. S. Lau, in *VLSI Electronics: Microstructure Science*, edited by N. G. Einspruch and G. B. Larrabee (Academic, New York, 1983), Vol. 6, Ch. 6.
[2]S. P. Murarka, *Silicides for VLSI Applications* (Academic, New York, 1983).
[3]S. P. Murarka, J. Vac. Sci. Technol. **17**, 775 (1980).
[4]F. M. d'Heurle, in *VLSI Science and Technology*, edited by C. Dell'Oca and W. M. Bullis (Electrochemical Society, Pennington, 1982), p. 194.
[5]J. L. Vossen, J. Vac. Sci. Technol. **19**, 761 (1981).
[6]F. Mohammadi, Solid State Technol. **1981**(1), 65.
[7]G. Ottaviani, J. Vac. Sci. Technol. **16**, 1112 (1979).
[8]S. P. Murarka, M. H. Read, C. J. Doherty, and D. B. Fraser, J. Electrochem. Soc. **129**, 293 (1982).
[9]S. Schiller, U. Heisig, K. Steinfelder, and Chr. Korndoerfer, Thin Solid Films **96**, 279 (1982).
[10]T. P. Chow, C. S. Grant, W. Katz, G. Gildenblat, and R. F. Reihl, J. Electrochem. Soc. **130**, 933 (1983).
[11]S. Inoue, N. Toyokura, T. Nakamura, and H. Ishikawa, J. Electrochem. Soc. **128**, 2402 (1981).
[12]F. Neppl, G. Menzel, and U. Schwabe, J. Electrochem. Soc. **130**, 1174 (1983).
[13]G. Beensh-Marchwicka, L. Kròl-Stepniewska, and W. Posadowski, Thin Solid Films **82**, 313 (1981).
[14]K. Steenbeck, E. Steinbeiss, and K.-D. Ufert, Thin Solid Films **92**, 371 (1982).
[15]M. Hill, Solid State Technol. **1980**(1), 53.
[16]D. M. Scott, thesis, California Institute of Technology, 1982.
[17]D. M. Scott, P. J. Grunthaner, B. Y. Tsaur, M-A. Nicolet, and J. W. Mayer, in *Proceedings of the Symposium on Thin Film Interfaces and Interactions*, edited by J. E. E. Baglin and J. M. Poate (The Electrochemical Society, Princeton, 1980), Vol. **80–2**, p. 148.
[18]D. M. Scott and M-A. Nicolet, Nucl. Instrum. Methods **182/183**, 655 (1981).
[19]L. S. Hung, L. R. Zheng, and J. W. Mayer, J. Appl. Phys. **54**, 792 (1983).
[20]L. Wieluński, D. M. Scott, M-A. Nicolet, and H. von Seefeld, Appl. Phys. Lett. **38**, 106 (1981).
[21]D. M. Scott, L. Wieluński, H. von Seefeld, and M-A. Nicolet, Nucl. Instrum. Methods **182/183**, 661 (1981).
[22]D. M. Scott and M-A. Nicolet, Phys. Status Solidi A **66**, 773 (1981).
[23]C.-D. Lien, M-A. Nicolet, and S. S. Lau, Phys. Status Solidi A **81**, 123 (1984).
[24]Chuen-Der Lien and Marc-A. Nicolet, in *Proceeding of MRS Symposium on Thin Film and Interfaces*, edited by J. E. E. Baglin, D. R. Campbell, and W. K. Chu (North-Holland, New York, 1984).
[25]N. W. Cheung, M-A. Nicolet, M. Wittmer, C. A. Evans, Jr., and T. T. Sheng, Thin Solid Films **79**, 51 (1981).
[26]M. Wittmer, C.-Y. Ting, I. Ohdomari, and K. N. Tu, J. Appl. Phys. **53**, 6781 (1982).
[27]I. Ohdomari, K. N. Tu, K. Suguro, M. Akiyama, I. Kimura, and K. Yoneda, Appl. Phys. Lett. **38**, 1015 (1981).
[28]M. Wittmer and K. N. Tu, Phys. Rev. B **27**, 1173 (1983).
[29]C. A. Crider, J. M. Poate, J. E. Rowe, and T. T. Sheng, J. Appl. Phys. **52**, 2860 (1981).
[30]F. Nava, S. Valeri, G. Majni, A. Cembali, G. Pignatel, and G. Queirolo, J. Appl. Phys. **52**, 6641 (1981).
[31]M. Wittmer, C.-Y. Ting, and K. N. Pu, J. Appl. Phys. **54**, 699 (1983).
[32]L. R. Zheng, L. S. Hung, and J. W. Mayer, Thin Solid Films **104**, (1983).
[33]C.-D. Lien, L. S. Wieluński, M-A. Nicolet, and K. M. Stika, Thin Solid Films **104**, 234 (1983).
[34]J. O. Olowolafe, M-A. Nicolet, and J. W. Mayer, J. Appl. Phys. **47**, 5182 (1976).
[35]P. Révész, J. Gyimesi, and É. Zsoldos, J. Appl. Phys. **54**, 1860 (1983).
[36]R. J. Schutz and L. R. Testardi, J. Appl. Phys. **50**, 5773 (1979).
[37]M. J. Rice, Jr. and K. R. Sarma, J. Electrochem. Soc. **128**, 1368 (1981).
[38]K. T. Ho, M-A. Nicolet, and D. M. Scott (private communication).

[39]K. T. Ho, C.-D. Lien, M-A. Nicolet, and D. M. Scott, in *Proceedings of MRS Symposium on Thin Film and Interfaces*, edited by J. E. E. Baglin, D. R. Campbell, and W. K. Chu (North-Holland, New York, 1984).
[40]J. Pelleg and S. P. Murarka, J. Appl. Phys. **54**, 1337 (1983).
[41]J.-S. Maa, C. W. Magee, and J. J. O'Neill, J. Vac. Sci. Technol. B **1**, 1 (1983).
[42]H. Norström, F. Runovc, R. Buchta, P. Wiklund, M. Östling, and C. S. Petersson, J. Vac. Sci. Technol. A **1**, 463 (1983).
[43]F. Jahnel, J. Biersack, B. L. Crowder, F. M. d'Heurle, D. Fink, R. D. Isaac, C. L. Lucchese, and C. S. Petersson, J. Appl. Phys. **53**, 7372 (1982).
[44]P. Pan, N. Hsieh, H. J. Geipel. Jr., and G. J. Slusser, J. Appl. Phys. **53**, 3059 (1982).
[45]M. Y. Tsai, H. H. Chao, L. M. Ephrath, B. L. Crowder, A. Cramer, R. S. Bennett, C. J. Lucchese, and M. R. Wordeman, J. Electrochem. Soc. **128**, 2207 (1981).
[46]S. P. Murarka and D. B. Fraser, J. Appl. Phys. **51**, 342 (1980).
[47]J. N. Ramsey, J. Vac. Sci. Technol. A **1**, 721 (1983).
[48]P. J. Grunthaner, F. J. Grunthaner, D. M. Scott, M-A. Nicolet, and J. W. Mayer, J. Vac. Sci. Technol. **19**, 641 (1981).
[49]K. T. Ho, M-A. Nicolet, and L. S. Wieluński, Thin Solid Films **104**, 243 (1983).
[50]T. Banwell, M-A. Nicolet, and D. M. Scott, Thin Solid Films **107**, 67 (1983).
[51]M. Wittmer and T. E. Seidel, J. Appl. Phys. **49**, 5827 (1978).
[52]M. Wittmer, C.-Y. Ting, and K. N. Tu, J. Appl. Phys. **54**, 699 (1983).
[53]M. Wittmer, C.-Y. Ting, and K. N. Tu, Thin Solid Films **104**, 191 (1983).
[54]M. Wittmer and K. N. Tu. Phys. Rev. B (in press).
[55]A. Kikuchi, J. Appl. Phys. **54**, 3998 (1983).
[56]K. T. Ho, C.-D. Lien, and M-A. Nicolet, J. Appl. Phys. (in press).
[57]K. T. Ho and M-A. Nicolet (private communication).
[58]C.-D. Lien, L. S. Wieluński, and M-A. Nicolet, Nucl. Instrum. Methods **213**, 463 (1983).
[59]J. B. Bindell, J. W. Colby, D. R. Wonsidler, J. M. Poate, D. K. Conley, and T. C. Tisone, Thin Solid Films **37**, 441 (1976).
[60]C. Canali, C. Catellani, M. Prudenziati, W. H. Wadlin, and C. A. Evans, Jr., Appl. Phys. Lett. **31**, 43 (1977).
[61]P. W. Lew and C. R. Helms, J. Appl. Phys. (in press).
[62]J. B. Bindell, W. M. Moller, and E. F. Labuda, IEEE Trans. Electron. Devices **ED-27**, 420 (1980).
[63]A. H. Hamdi, F. D. McDaniel, and S. R. Wilson (to be published).
[64]S. S. Cohen, P. A. Piacente, G. Gildenblat, and D. M. Brown, J. Appl. Phys. **53**, 8856 (1982).
[65]C. Y. Wei, W. Kate, and G. Smith, Thin Solid Films **104**, 215 (1983).
[66]A. Kikuchi and S. Sugaki, J. Appl. Phys. **53**, 3690 (1982).
[67]A. Guldan, V. Schiller, A. Steffen, and P. Balk, Thin Solid Films **100**, 1 (1983).
[68]F. A. d'Avitaya, G. Bomchil, and C. Arena (private communication).
[69]C. Canali, F. Catellani, G. Ottaviani, and M. Prudenziati, Appl. Phys. Lett. **33**, 187 (1978).
[70]T. J. Kingzett and C. A. Ladas, J. Electrochem. Soc. **122**, 1729 (1975).
[71]R. J. Blattner, C. A. Evans, Jr., S. S. Lau, J. W. Mayer, and B. M. Ullrich, J. Electrochem. Soc. **122**, 1732 (1975).
[72]M. Severi, E. Gabilli, S. Guerri, and G. Celotti, J. Appl. Phys. **48**, 1998 (1977).
[73]P. Joubert, P. Auvray, A. Guivarc'h, and G. Pelous, Appl. Phys. Lett. **31**, 753 (1977).
[74]S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1982).
[75]P. B. Ghate, Thin Solid Films **93**, 359 (1982).
[76]J. J. Gajda and H. S. Wildman, IEEE Proceedings of the 20th Reliability Physics Symposium, 1982.
[77]L. S. Wieluński, C.-D. Lien, B. X. Liu, and M-A. Nicolet, J. Vac. Sci. Technol. **20**, 182 (1982).
[78]H. Föll and P. S. Ho, J. Appl. Phys. **52**, 5510 (1981).
[79]C.-D. Lien, M-A. Nicolet, and P. William, Thin Solid Films (submitted).
[80]L. S. Wieluński, C.-D. Lien, B. X. Liu, and M-A. Nicolet, in *Metastable Materials of Formation by Ion Implantation*, edited by S. T. Picraux and W. J. Choyke (Elsevier, New York, 1982), Vol. 7, p. 139.
[81]P. Joubert, P. Auvray, and L. Henry, Thin Solid Films **79**, 235 (1981).
[82]R. W. Bower and J. W. Mayer, Appl. Phys. Lett. **20**, 359 (1972).
[83]S. M. Goodnick, M. Fathipour, D. L. Ellsworth, and C. W. Wilmsen, J. Vac. Sci. Technol. **18**, 949 (1981).
[84]M. A. Taubenblatt and C. R. Helms, J. Appl. Phys. **53**, 6308 (1982).
[85]R. Butz, G. W. Rubloff, and P. S. Ho, J. Vac. Sci. Technol. A **1**, 771 (1983).
[86]S. Yanagisawa and T. Fukuyama, J. Electrochem. Soc. **127**, 1150 (1980).
[87]D. J. Silversmith, D. D. Rathman, and R. W. Mountain, Thin Solid Films **93**, 413 (1982).
[88]C. S. Wu, S. S. Lau, T. F. Kuech, and B. X. Liu, Thin Solid Films **104**, 175 (1983).
[89]S. S. Lau, C. S. Pai, C. S. Wu, T. F. Kuech, and B. X. Liu, Appl. Phys. Lett. **41**, 77 (1982).
[90]T. P. Chow, D. H. Bower, R. L. Van Art, and W. Katz, J. Electrochem. Soc. **130**, 952 (1983).