PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980 J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 1067–1070

INITIAL STAGE OF METAL/Si INTERFACE FORMATION AT ROOM TEMPERATURE

Kazuhiko Okuno, Motohiro Iwami and Akio Hiraki

Department of Electrical Engineering Osaka University Suita, Osaka Japan

Room temperature interfacial intermixing reaction between Au or Ni(film) and Si(substrate) was studied as a function of metal-film thickness by AES, ELS and LEED under slow deposition condition(0.1= 0.3 monolayer/min) at ultra high vacuum(\sim 5x10⁻¹⁰ Torr). Metal-film more than a critical thickness (\sim 2 monolayers) reacts intermixingly with Si-substrate to give rise to metallic alloy, where the change in the electronic state of Si was clearly observed in $-d^2N/dE_K^2$ spectrum of AES.

I. Introduction

Formation of metal/semiconductor(M/S) interfaces is crucial in semiconductor device technology, e.g. the Schottky barrier forma-tion. It has been reported that when metal film(~500Å) such as Al, Au and so on, are vacuum evaporated onto clean surfaces of (covalent) semiconductors with energy gaps(E_g 's) less than ~2.5eV[or dielectric constants(ϵ 's) larger than ~8], for example, Si, they react at the interfaces with each other and very thin alloyed layer (~200Å) is introduced readily even at room temperature[1]. In order to induce an instability in covalent bondings of semiconductors to result in the intermixing reaction, a metal which have the ability to screen Coulomb interaction due to its mobile free electrons must play an important role[2]. In fact, non-metal films on these semiconductors, for example, Ge(film) on Si(substrate), do not induce any interfacial intermixing reactions[3]. There is a proposal on the origin of the low temperature interfacial intermixing reaction by considering the positive role of a metal[4]. In order to study the origin of such an interfacial intermixing reaction at M/S contacts, we investigated M/S systems under the controlled deposition of a metal film onto a clean Si(111) surface by Auger electron spectroscopy(AES), low energy electron loss spectroscopy(ELS) and low energy electron diffraction(LEED).

II. Experimental

Surfaces of phosphorus doped n-type Si(111) wafers with resistivity of 6-9 ohm cm were cleaned by flush heating at ~1200 °C under ultra high vacuum(~2x10⁻¹⁰ Torr). Contaminants on the surface(carbon in this case) were examined by AES to be less than 0.1% of surface Si atoms. The AES(dN/dE_K and $-d^2N/dE_K^2$; E_K is the kinetic energy of electrons), ELS($-d^2N/dE_K^2$) and LEED experiments were performed under slow deposition condition(0.1-0.3 monolayer/min) of a metal onto clean Si(111) surfaces in ultra high vacuum[~5x10⁻¹⁰ Torr

under Au(or Ni) deposition] at room temperature. Modulation voltage for the differentiation was 0.8V(p-p). One monolayer of a metal film was defined as one deposit atom per Si atom on the Si(lll) surface, i.e. 7.9×10^{14} cm⁻².



III. Results and Discussion

Fig.1 AES[(a)-(d)], dN/dE_K , and ELS[(e)-(i)], $-d^2N/dE_K^2$, spectra of a Au/Si specimen with different Au-film thickness

Figure 1 shows AES[(a)-(d)] and ELS[(e)-(i)] spectra of a Au(film)/ Si(substrate) specimen with different Au-thickness[5]. A brief summary of the results in Fig.1 is as follows. Surface states characteristic to Si (111) clean surface disappeared at ~1 monolayer and a new electronic state were introduced. The interfacial intermixing reaction occurred for Au-film with thickness more than ~5 monolayers, whereas Au-film with thickness less than ~2 monolayers was stable for the reaction.

In order to clarify the initial stage of the intermixing reaction at M/S contacts, we performed the detailed examination of Si(LVV) Auger

spectra with different Au-film thickness in hope that it would bear new and important informations on the electronic structure of the valence electrons of Si. Therefore, we examined the second derivative $(-d^2N/dE_K^2)$ spectrum of Si(LVV) Auger electrons because it usually developes fine structure in N(E_K) and peaks in it correspond to peaks, including shoulder, in N(E_K). The experimental results for Au/Si system with different Au-thickness are shown in Fig.2. One can see that Si(LVV) Auger spectrum begins to change its shape at ~3 monolayers[Fig.2(b)].

Here, it may be necessary to show what can be said from the spectral change in the Si (LVV) Auger spectrum. For the convenience of the understanding of this estimation, LVV Auger spectra[N(E_K), dN/dE_K and $-d^2N/dE_K^2$] of Si are shown in Fig.3. By the way, Si(LVV) Auger spectrum contains informations on both electrons in L-shell and valence electrons of Si[n(E)] — mainly p-like electrons[6]. However, it can be considered that the change in the shape[N(E_K)] of Si(LVV) Auger spectrum is mainly due to that in valence electrons because a change in E_L will induce little effect on the spectral shape. Kinetic energy (E_K) of LVV Auger electrons is roughly ex-



Fig.2 $-d^2N/dE_K^2$ spectra of a Au/Si specimen with different Au-film thickness



Fig.3 Auger spectra of Si(LVV): (a) $N(E_K)$, (b) dN/dE_K and (c) $-d^2N/dE_K^2$. Solid curves are typical spectra of pure Si. Dotted curves are expected ones due to the increase in $N(E_K)$ in larger E_K region

pressed as

 $E_{K} = E_{L} - 2E_{V}.$ --- (1) Here, E_L is the binding energy of L-shell electron and E_V the average binding energy of two valence electrons involved in the Auger transition. Though Si(LVV) Auger spectrum $[N(E_K)]$ will not directly reflect a state density[n(E)] itself in valence band of Si but mainly its self-convolution, the valence band structure near $E_F(or the top of valence$ band: E_0) of Si can be qualitatively deduced from the change in the shape of $N(E_K)$ of Auger signals at large EK region because the self-convolution is limited within the narrow energy region near E_{O} . From eq.(1) it can be said that the relative increase in the number of Si(LVV) Auger electrons with larger E_{K} will result in the spectral changes in

 $-d^2N/dE_K^2$ with the following characteristics: (i) energy shift of the negative peak to larger E_K and (ii) the appearance of a new shoulder as illustrated in the dotted curve in Fig.3(c), where the main structure in the smaller E_K region is kept unchanged to avoid confusion.

Now, back to Fig.2, it can be said that the Au-deposition of ~3 monolayers gives rise to a shift in the energy of the negative peak to larger E_K from 93 to 94.5eV[Fig.2(a)-(b)], or the broadening in the dN/dE_K like that of Fig.1(c). From the expected change in the Auger signals shown in Fig.3, it can be said that ~3 monolayers of Au-film induced the increase in the density of state of valence electrons of Si with lower binding energy, i.e. the increase in n(E) near Fermi energy(E_F). Corresponding to the increase in n(E) near E_F , a shoulder appeared in $-d^2N/dE_K^2$ spectra at large E_K region. The



Fig.4 K $_{\beta}$ -emission spectra from pure Si(dotted curve) and Si-Au(20 at.%) alloy (solid one)

shoulder grew up with increasing Au= film thickness to ~5 monolayers[Fig.2 ,(c)], and finally changed its shape into a clear peak at the stage of Au= film with ~12 monolayers[Fig.2,(d)]. Si(LVV) Auger spectrum(dN/dE_K) corresponding to Fig.2, (d) is the double peaked one[like Fig.1,(d)] which is characteristic to Si in metastable Si-Au alloy[7]. The existence of the peak at 95eV in the double peaked spectrum of dN/dE_K , whose energy position is larger than that of the peak at 92eV in dN/dEK of pure Si, also shows that a Si atom in the metastable Si-Au alloy has higher state density near EF in pure Si. We named such a Si to be 'metallic' one[7]. The metallic nature of 3p= electrons was clearly observed in the SXS result of Si in Si-Au alloy and



Fig.5 Schematic illustration of the room temperature interfacial intermixing reaction for the Au slow deposition on crystalline Si

pure Si[8]. As shown in Fig.4, K β -emission spectra , which reflect the local density of state of $3p_{\pm}$ electrons at Si site, indicate that Si atoms in Si (20 at%)-Au alloy, which corresponds to Fig.1,(d) and Fig.2,(d), have high state density of 3p-electrons at E_F compared with those in pure crystalline Si. Therefore, it can be said that the Au-deposition of ~3 monolayers[Fig.2,(b)] induces the relative increase of the local density of states[n(E)] near E_F. Namely, the interfacial intermixing reaction between Au-film and Si-substrate begins to start at this stage of Au-coverage at room tempera-

ture.

The above experimental results of Au slow deposition on a clean Si (111) surface can be explained as shown schematically in Fig.5. Deposited Au-film less than ~2 monolayers does not function as a metal, and therefore it does not react intermixingly with Si-substrate[Fig.5,(a)]. Once the thickness of the deposited Au-film exceeds ~2 monolayers[Fig.5,(b)] — the critical thickness for Au-Si system — , it functions as a metal to induce the instability of covalent bondings of Si atoms in the surface region of Si-substrate to react intermixingly with Si at room temperature[Fig.5,(c)]. Therefore, the existence of the critical thickness for Au-film to react intermixingly with Si-substrate indicates the importance of the role of a metal for the room temperature interfacial intermixing reaction[1]. Similar result was observed in the slow deposition experiment of Ni onto Si surface, i.e. metallic alloy(Ni-silicide) formation on the surface of the specimen.

Therefore, the problem of the Fermi level pinning of Schottky barriers, which has been examined experimentally and theoretically by many groups[9], should be examined and discussed carefully by considering the presence of the intermixing reaction in some M/S systems.

References

- 1) A.Hiraki, K.Shuto, S.Kim, W.Kammura and M.Iwami: Appl. Phys. Lett. 31 (1977) 611.
- 2) P.W.Anderson: Elementary Excitation in Solids, Molecules and Atoms, PartA, Plenum Press (1974).
- 3) A.Hiraki, K.Okuno, T.Ito, S.Kim and M.Iwami: to be published.
- 4) A.Hiraki: J. Electrochem. Soc. (in press).
- 5) K.Okuno, T.Ito, M.Iwami and A.Hiraki: Solid State Commun. 34 (1980) 493.
- 6) D.R.Jennison: Phys. Rev. Lett. 40 (1978) 807.
- 7) A.Hiraki, A.Shimizu, M.Iwami, T.Narusawa and S.Komiya: Appl. Phys. Lett. 26 (1975) 57.
- 8) K.Tanaka and A.Hiraki: Proc. Intern. Conf. X-ray and XUV Spectroscopy, Jpn. J. Appl. Phys., Suppl. 17-2 (1978) 121.
- See, for example, including its references, I.Lindau, P.W.Chye, C.M.Garner, P.Pianetta, C.Y.Su and W.E.Spicer: J. Vac. Sci. Technol. 15 (1978) 1332.