Electronic Promotion of Silicon Nitridation by Alkali Metals

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We report the first observation of a catalytic nitridation of a semiconductor with molecular nitrogen. The Si(100)2×1 surface modified by a sodium monolayer was studied by core-level and valence-band photoemission spectroscopy and work-function measurements using synchrotron radiation. At room temperature, the exposure to molecular nitrogen resulted in Si—N bond formation. The sodium is removed from the surface by thermal desorption at moderate temperature leading to the formation of a clean Si_3N_4-Si interface at a much lower temperature than without the alkali metal.

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Nitridation of semiconductor surfaces is an interesting and challenging problem from the fundamental as well as from the technological point of view. In the last years, there has been an increasing interest in the study of the nitridation of silicon, driven by its potential application in device technology, which still poses many unsolved problems. Since the nitrogen molecule has a higher energy of dissociation than oxygen, it makes an interaction with a silicon substrate more difficult. These difficulties have directed the effort to promote silicon nitridation by interaction with other nitrogen-containing molecules, like ammonia, which in contrast to nitrogen has a significant sticking coefficient on silicon.[1-3] The process could then be assisted by irradiation with an electron beam[1] or an intense photon beam such as the unmonochromatized "white light" emitted by a synchrotron radiation source.[3] However, these processes could damage the surface. At room temperature, nitrogen has a negligible sticking coefficient on silicon. Maillot, Roulet, and Dufour[4] obtained silicon nitridation by ion bombardment with nitrogen. If such a procedure results in the formation of a Si_3N_4-Si interface, it also heavily damages the surface.

Since alkali metals have recently proved to be efficient electronic promoters of semiconductor oxidation,[5] it is challenging to investigate whether the catalytic promotion by alkali metals could be an alternative approach to silicon nitridation. This problem is particularly interesting considering the fact that it is much more difficult to dissociate molecular nitrogen than molecular oxygen.

In this Letter, we show what we believe is the first example of catalytic nitridation of a semiconductor. A Si(100)2×1 surface modified by a sodium monolayer exhibits the formation of Si—N bonds at room temperature when exposed to molecular nitrogen. Furthermore, by mild thermal annealing, the catalyst is removed by thermal desorption, and a Si_3N_4-Si interface is formed at much lower temperature than with direct thermal nitridation.[6] This further illustrates the unique catalytic properties of alkali metals.

The experiments were performed on the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin–Madison. Research-grade nitrogen was used for N_2 exposures. All the other experimental details are given elsewhere.[5]

The growth of the SiN_x complex can be followed by looking at the Si 2p core-level chemical shift. Figure 1 displays the Si 2p core-level spectra of a Si(100) surface covered with a monolayer of sodium, followed by exposures at room temperature to 3000 and 7500 L [1 L (langmuir) $=10^{-6}$ Torr sec] of molecular nitrogen, and finally subjected to several annealings at increasingly higher temperatures between 450 and 650 °C. As evident from Fig. 1, the exposure to molecular nitrogen at room temperature leads to the growth of a new peak A shifted to higher binding energy by 0.7 eV in comparison with the Si 2p core level. Peak A is related to the formation of Si—N bonds and indicates the growth of a SiN_x compound as reported for the thermal nitridation of silicon[7] at temperatures above 1000 °C.[6,7] For comparison, the same N_2 exposures on a sodium-free Si(100) surface did not result in any change for the Si 2p core level. This clearly indicates the role of sodium as promoter of silicon nitridation.

When the surface is annealed at temperatures from 450 to 650 °C, a new chemical shift (2.6–3 eV) of the Si 2p core level is observed (peak B in Fig. 1). This peak, which is the dominant new feature of the spectrum, cor-

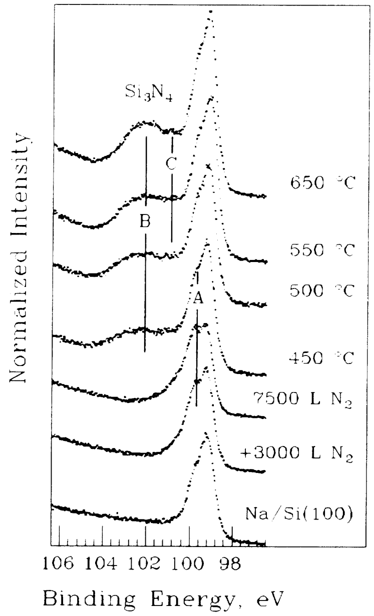

FIG. 1. N_2/(1 ML Na)/Si(100)2×1. Photoemission spectra showing the Si 2*p* core level after increasing annealing temperatures at a photon energy of 130 eV.

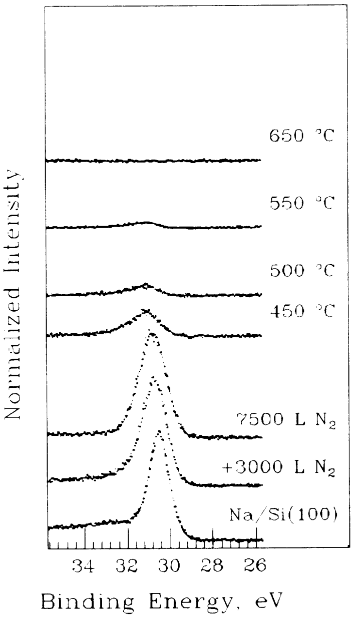

FIG. 2. N_2/(1 ML Na)/Si(100)2×1. Photoemission spectra showing the Na 2*p* core level after increasing annealing temperatures at a photon energy of 82 eV.

responds to the formation of Si_3N_4 on the silicon surface as reported by Maillot, Roulet, and Dufour.[4] Finally, another smaller peak, *C*, appears above 550 °C, shifted by 1.7 eV from the Si 2*p* core level. By analogy with the results on silicon oxides,[5,8] one finds that peak *C* corresponds to silicon atoms bonded to three nitrogen atoms.[4] This indicates that the Si_3N_4-Si interface is not abrupt.

Figure 2 shows the behavior of the Na 2*p* core level for the same sequences. The exposures to 3000 and 7500 L of molecular nitrogen lead to an approximate 50% broadening of the Na 2*p* core level. This indicates some kind of interaction between sodium and nitrogen. When the surface was subjected to annealing at temperatures between 450 and 650 °C, the intensity of the Na 2*p* decreased and reached zero at 650 °C. This indicates that the sodium has been removed from the surface by thermal desorption as observed previously in the case of the catalytic oxidation of silicon by alkali metals.[5] The temperature dependence of the various components are plotted in Fig. 3. One can see that the intensity decrease of the sodium core level versus the annealing temperature is linear. The line reaches zero intensity at a temperature $T_d = 575\,°C$, which indicates that the last experimental point at 650 °C is above the temperature of total sodium desorption. Therefore, $T_d = 575\,°C$ should be considered as the temperature above which the sodium is totally removed from the surface. The linear decrease of the sodium coverage versus the temperature confirms that sodium is removed by desorption and not by diffusion through the surface, which would not give the observed linear decrease. This observation is consistent with the property that, in contrast to other metals,[9] alkali metals (except lithium) do not interdiffuse through the silicon surface or form silicides.[5,10] During the entire nitridation sequence, the sodium layer does remain "on top" and the Si_3N_4 grows underneath, i.e., at the Na/Si interface. This point is further confirmed by the fact that silicon nitrides such as Si_3N_4 are well known to be alkali-

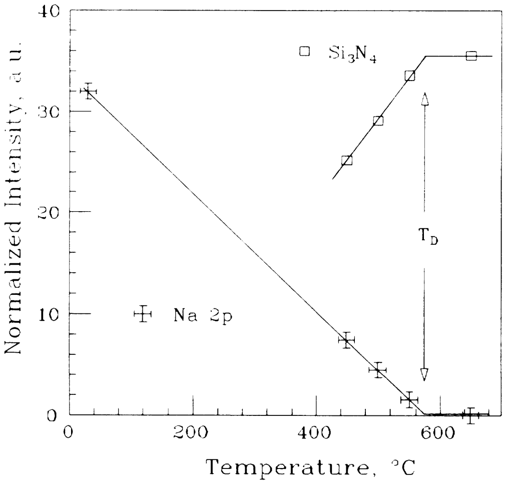

FIG. 3. Intensity of the Na 2*p* core level vs annealing temperature for the (7500 L N_2)/(1 ML Na)/Si(100)2×1 system. The intensity of the Si_3N_4 peak (*B*) normalized to the intensity of the Si 2*p* peak is also shown.

metal diffusion barriers.[11] Therefore, if the nitride was not formed at the Na/Si interface, sodium could not escape and be removed by thermal desorption.

Figure 3 also displays another important feature of the silicon nitridation process, namely, the intensity variation with temperature of the Si_3N_4 peak relative to the Si $2p$ one. Interestingly, it increases linearly with the temperature until T_d, the temperature of total desorption. This indicates that the amount of nitride grows with temperature when sodium is still present on the surface, and shows that saturation was not reached in this experiment. The nitride growth stops when the alkali metal is totally removed by thermal desorption. This further emphasizes the role of sodium as an electronic promoter of silicon nitridation.

A complementary view of the nitridation process is given by the study of the valence band. Figure 4 shows the valence-band spectra for the Na/Si(100)2×1 system exposed at room temperature to molecular nitrogen and then subjected to several annealings at temperatures between 450 and 650°C. The clean spectrum of Na/Si(100)2×1 exhibits a peak E_1 which corresponds to emission from the Si $3p$ level. Its binding energy is 0.5 eV higher on the sodiated silicon (100) surface than on the clean one. With an exposure to 3000 L of molecular nitrogen, two new peaks E_2 and E_3 arise and are related to the nitrogen $2p$ levels. Peak E_2, which has not been observed previously on metal surfaces, partially overlaps with peak E_1. Interestingly, the binding energy of peak E_3 corresponded to the value observed for N_2/Fe(111).[12] After an N_2 exposure of 7500 L, the intensity of peak E_3 is increased while that of peak E_2 remains about the same. This corresponds to a simultaneous increase of the intensity of peak A (Fig. 1) which indicates the formation of Si—N bonds and the subsequent growth of SiN_x compound on the surface. It is likely that at room temperature, the silicon nitridation cannot take place without the presence of atomic nitrogen. Therefore, in analogy with oxygen,[13] peak E_3 is interpreted as being due to atomic nitrogen while peak E_2 is likely to correspond to the molecular species (an alternative explanation for peak E_2 with the formation of Si—N bonds is given in Ref. 2). These results indicate that sodium enhances dramatically the nitrogen sticking coefficient, and dissociates the molecular nitrogen.

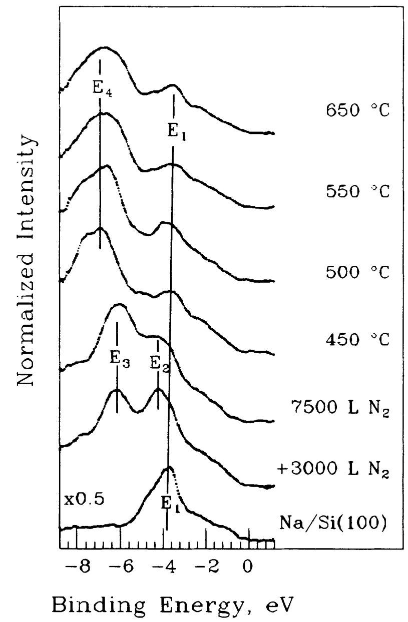

FIG. 4. N_2/(1 ML Na)/Si(100)2×1. Valence-band photoemission spectra with increasing annealing temperatures, at a photon energy of 82 eV.

The onset of Si_3N_4 formation appears in the valence-band spectra of Fig. 4 as a dominating E_4 structure at annealing temperatures between 450 and 650°C. This assignment is confirmed from the Si $2p$ chemical shift (Fig. 1), and further is in agreement with previous valence-band studies of Si_3N_4.[2,7] After sodium removal from the surface by thermal desorption, peak E_1 is shifted back to its initial lower binding-energy position for the clean (sodium free) silicon surface.[14]

Finally, the last experimental feature comes from the measurement of the work-function changes with molecular nitrogen. Interestingly, the adsorption of nitrogen on the sodiated Si(100) surface (whose work function decreased by 3 eV[14] after deposition of one Na monolayer) induced only a small additional decrease of the work function by 0.2 eV at the onset of nitridation as compared with 0.55 eV with oxygen at the onset of oxidation.[14] This is in agreement with a lower polarizability of the nitrogen molecule resulting in its higher dissociation energy compared with the oxygen molcule.

The above experimental results support the picture of sodium as an electronic promoter of silicon nitridation which (i) enhances dramatically the sticking coefficient of molecular nitrogen, (ii) dissociates the nitrogen molecule, and (iii) weakens the silicon backbonds. The crucial role of sodium in the nitridation process is further stressed by the fact that the growth of the Si_3N_4 stops abruptly at the temperature T_d corresponding to the total desorption of sodium (Fig. 3). Our results also reflect a dynamic equilibrium between the Si_3N_4 rate of growth which increases with temperature and the amount of sodium catalyst left at the surface which decreases with temperature.

Apparently, the catalytic nitridation of the silicon surface by alkali metals is a more complex process than the corresponding catalytic oxidation. While all alkali metals show a similar catalytic activity for silicon oxidation,[5] the full nitridation is achieved selectively by sodium. With potassium, room-temperature nitridation was achieved with Si—N bond formation, but only very small amounts of Si_3N_4 were grown by thermal annealing. This is possibly related to structural differences such as the atomic radius of the alkali-metal adsorbates and the alkali-substrate distance which could also be of relevance in this context.

In conclusion, we have shown the first example of catalytic nitridation of a semiconductor using sodium as catalyst. While sodium was removed from the surface by thermal desorption at a moderate temperature, a clean (sodium free) Si_3N_4-Si interface was formed at much lower temperature than by direct thermal annealing. This study emphasizes the unique and versatile role of alkali metals in the electronic promotion of surface reactions.

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