THIN FILM KINETICS AND REACTIONS AT METAL-SILICON INTERFACES

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Raman scattering and RBS measurements are used to characterize the initial interactions at metal-Si interfaces. The results indicate that for some metals, a disordered intermixed layer can precede the formation of an ordered silicide. The results are discussed in terms of the chemical energy and strain which result from the interdiffusion.

Introduction

The interactions at metal-silicon interfaces have been the focus of both structural and electronic property studies. The junction is known to lead to Schottky barrier formation, but the detailed origin of this effect is still unresolved. While the interactions that lead to Schottky barrier formation occur over the scale of ~20 Å or less, in contrast, solid-state reactions extending over >100 Å are required to form the silicide layers which are of technological importance. In this study we will focus on the initial interactions at the interface and how they relate to the formation of both the Schottky barrier and the stable silicide films.

The "near noble" metals of Ni, Pd, and Pt are often used to study both Schottky barrier formation and interface reactions. These metals are known to react with Si at low annealing temperatures to form metal-rich silicide compounds (M_2Si), but higher temperature annealing leads to the formation of silicon-rich silicide compounds (MSi or MSi_2). The solid solubility, however, of the M in the Si or the Si in the metal is, in general, limited to less than 1%. In this study, results for Ni, Pd and Pt will be discussed, and compared to initial reactions of Ti films on Si.

The limited solubility of the constituents thus provides a barrier to the formation of the silicide; atomic interdiffusion cannot result in local compositions similar to that of the silicide compound. An alternative to this restriction is that a disordered layer is formed with a composition similar to the silicide. The crystalline silicide compound would grow from nucleation sites in the disordered region. In this study, evidence is presented which indicates that for some conditions, disordered intermixing precedes silicide formation. The conditions which lead to the disordered phase are discussed in terms of the free energy of the system.

The experimental results include Raman scattering and Rutherford backscattering. The Raman scattering experiments utilize both the interference enhanced Raman scattering configuration (IERS) and standard backscattering Raman configurations. The RBS measurements utilize channeling and glancing exit angle and standard RBS. The IERS, channeling and glancing exit angle experiments have sensitivities to less than 20 Å while the standard Raman and RBS are useful for films thicker than 50 Å.

Experimental

The Ni, Pd, Pt or Ti films were deposited in an oil-free deposition system or in a UHV system. The base pressure for the oil-free system was 5×10^{-8} Torr, and the samples were either chemically

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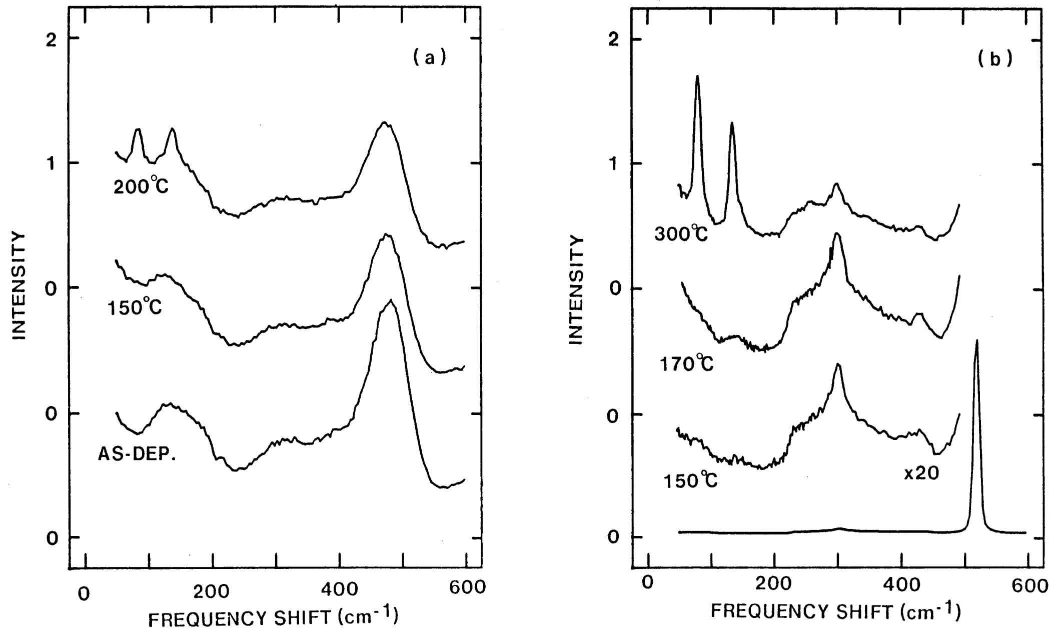

Fig. 1. The Raman spectrum of Pt (50 Å) on a-Si:H obtained using the IERS technique, (a), and Pt (80 Å) on Si<100> obtained using standard backscatter configuration (b). The annealing temperatures are indicated.

etched before loading or freshly prepared amorphous Si. The base pressure of the UHV system was 1 x 10^{-10} Torr and the samples were sputter cleaned and annealed. Raman scattering measurements were carried out *in situ* in the UHV system while a separate vacuum annealing oven was used for samples prepared in the oil-free system. For the Ti sample which was prepared in the oil-free system, a 20 Å a-Si cap was deposited before removal from the system. The sample was annealed and Raman spectra obtained in the UHV system. In all cases described here 50 to 80 Å of metal was deposited. The details of the IERS and standard Raman scattering configurations are described elsewhere.[1]

Results and Discussion

The Raman results for Pt deposited on a-Si:H and crystalline Si are displayed in Fig. 1. The results of the Pt/a-Si:H interface were obtained using the IERS technique while the Pt/Si<100> results were obtained in the standard backscatter configuration. In both cases two sharp lines appear at ~90 and ~140 cm^{-1} after annealing to 200°C. These lines are attributed to the formation of crystalline silicide compounds.[2,3] At temperatures below 200°C there is evidence of Si diffusion from Auger and photoemission spectroscopy.[4,5] A broad featureless background is evident in the Raman spectra of the Pt/a-Si:H sample which we attribute to the intermixing. The broad featureless component is an indication of a disordered state. The effect of an amorphous structure in the Raman spectra is also evident in Fig. 1 where a sharp line is observed at 520 cm^{-1} for crystalline Si while a broad spectrum similar to the density of states is observed for the amorphous Si spectrum. RBS results of the same samples also show evidence of interdiffusion, but it is difficult to determine the composition of the intermixed region from the measurement.[6]

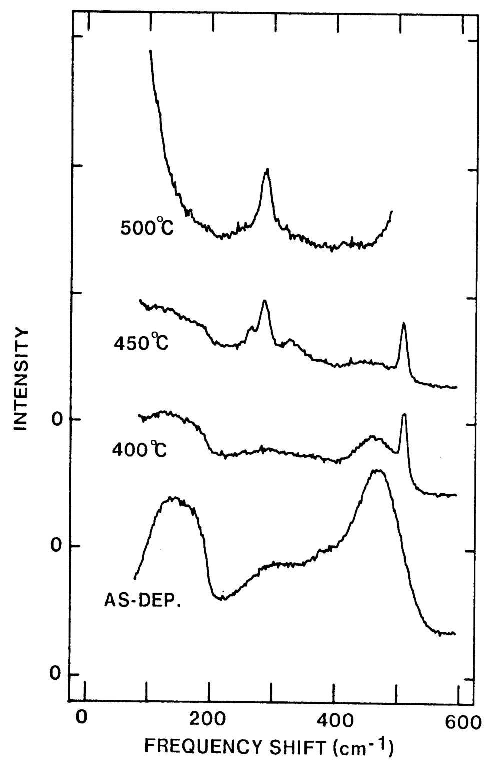

Fig. 2. The Raman spectrum of Ti (50 Å) on a-Si:H obtained using the IERS technique.

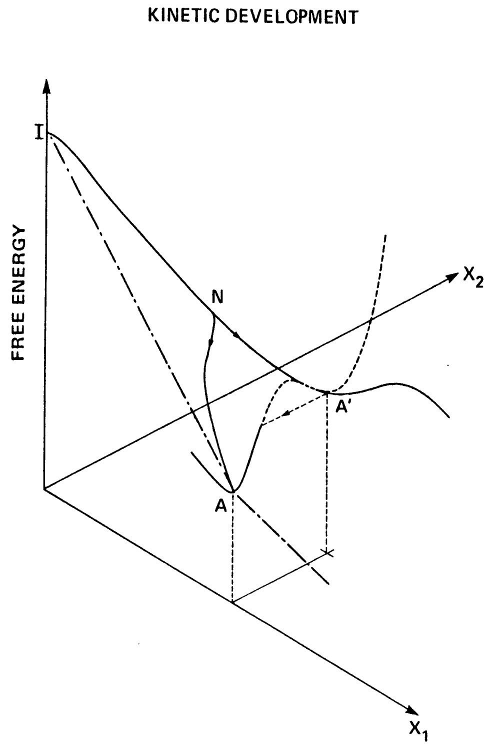

Fig. 3. A representation of the free energy evolution for metal-silicon solid state reactions. X_1 represents the degree of interdiffusion, X_2 the strain, A a stable silicide, A′ a metastable disordered state, and N a nucleation event.

The Raman and RBS measurements on Ni/Si show results very similar to the Pt/Si results. In this case, Ni_2Si is detected at an annealing temperature of 200 to 250°C. In contrast, it has been previously shown that crystalline Pd_2Si forms at the interface of Pd and Si immediately after room temperature deposition.

The Ti/Si systems behave somewhat differently from the "near noble" metals. Raman scattering results obtained in the IERS configuration are shown in Fig. 2. The as deposited spectrum reflects the features due to e-beam evaporated a-Si. While Ti is known to exhibit a weak feature at ~140 cm^{-1},[7] the feature is not clearly discernible because of the contribution due to the a-Si at the same frequency region. At an annealing temperature of 400°C a dramatic change in the spectrum is observed. The features due to the a-Si become weaker and broaden significantly; furthermore, a sharp line is observed at ~520 cm^{-1} which is attributed to crystalline Si. At 450°C several sharp features are observed from 250 to 350 cm^{-1}. The stronger feature at ~290cm^{-1} is attributed to a silicide tentatively identified as Ti/Si while the weaker features apparently reflect the formation of Ti_2O_3.[7]

The spectral changes of the Ti/Si interface observed at 400°C are indicative of considerable interdiffusion. It is apparently predominantly Si diffusion which can nucleate crystalline Si islands, and these regions are responsible for the sharp line at 520 cm^{-1}. Then at higher temperature silicide formation occurs.

The atomic interdiffusion is predominantly driven by the change in chemical energy due to the formation of M–Si bonding configurations. The diffusion process is, of course, a random process. This will lead to local environments which represent significant distortions from any of the ideal crystalline environments. The distortion can be characterized as a local strain. We suggest that it is possible that the significant random atomic interdiffusion at the interface can lead to the formation of a disordered or amorphous region.

The free energy of the system can then be described in terms of the atomic intermixing and the strain of the local atomic bonding configurations. The evolution of the interaction region can be defined in a configurational free energy diagram with two axes. Fig. 3 displays possible paths to which the system might evolve. Here point I represents the initial unreacted state, while state A represents the first stable silicide compound. The axis X_1 represents the degree of intermixing. This will result in a decrease in the chemical energy. Because of the random process of the diffusion, strain will build up, and the system could evolve to state A' which represents a disordered state. The minimum in the diagram at A' is probably realistic since there are metallic-glasses with compositions similar to that of the crystalline silicide compound.

Clearly the path that a system evolves is dependent on the temperature and other aspects reflected in the initial preparation conditions. Another possibility is represented by point N. This represents a nucleation of the crystalline silicide. Depending on the material properties, N may occur very near to the initial state, and this may represent the conditions for Pd/Si where silicide formation is observed immediately after deposition. For the other metals studied here (Ni, Pt, and Ti) it seems that a path which includes the metastable state A' is appropriate.

The model represented in Fig. 3 can serve as a guide to the relative importance of chemical stabilities and local distortions. Additionally, insight into effects like the template method of epitaxial silicide formation can be gained.[8] In this method, a thin layer of metal is deposited and initially reacted before further deposition. This would correspond to moving the nucleation point N to very near I and would essentially eliminate the homogeneous nucleation which could result from a disordered interface region.

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