The H₂ Plasma Treatment of Silver Contacts: Impact on Wire-Bonding Performance

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The ultrasonic wire-bonding performance on Ag bond pads is limited by the presence of oxides and organic contaminants. These contaminations act as lubricants during wire bonding. They reduce the interfacial friction and decrease the heat dissipation between the two contacting materials, leading to bad bond quality. Plasma processes have proven to be a valuable tool for eliminating such contaminations and boosting wire-bonding performance. We present investigations of the effects of H₂ plasma on oxidized silver films by photoelectron spectroscopy and quartz-crystal microbalance (QCM) measurements. The H₂ plasma treatment of Ag bond pads is not a classical surface-cleaning process. It is a bulk process, and it induces a reduction of silver oxide and recrystallization. The high mass transport caused by large changes in density during reduction leads to the formation of (111)-terminated regions at the surface. This densely packed termination can account for the apparent passivating effect of H₂ plasmas on Ag bond pads, which allows for long-term storage in ambient atmosphere without deteriorating bonding performance.

Key words: Ag contacts, H₂ plasma treatment, wire bonding

INTRODUCTION

Wire bonding is a standard process used in the semiconductor industry to connect the chip die to external leads. Thermosonic-tailless ball bonding (more commonly referred simply as ball bonding) uses an ultrasonic-piezo horn that excites a micrometer-sized gold ball pressed on the bond pad. The resulting local pressure at the regions in contact is in the GPa range and is, therefore, plastic. A schematic drawing of the contact region is depicted in Fig. 1. The heat produced by the friction under the lateral movement of the piezo actuator leads to a rise in local temperature in the asperities in contact. If the dissipated energy at the interface is high enough, pronounced interdiffusion leads to welding of the gold-ball contact region with the bond-pad material. The evolution of the contact-region morphology with time was experimentally investigated by Carrass and Jaecklin.¹

Under non-ultra-high vacuum (UHV) conditions, metals are covered by a thin (several nanometers)

organic contamination layer. Such contamination can reduce friction and act as a boundary lubricant² and, therefore, limit the frictional heating at the interface, leading to severely reduced bonding quality. Oxides on the surface can also reduce the frictional heating process or limit the interdiffusion of the elements in contact. This might lead to delamination and, therefore, higher cost. Kong and Ashby have investigated the thermodynamics of sliding interfaces in high-pressure contacts.³

The accepted limit for bond failure is below 1 ppm. Further improvements demand a better understanding of the tribological interface to improve process parameters and reduce costs. Therefore, for improved bondability characteristics, a method for removing the contaminants without damaging the delicate electronic devices is needed.

Plasmas can be used for surface cleaning/conditioning but also offer a much wider variety of industrial applications.⁴ In plasma, the process gases are excited by an external energy source. The adsorption of energy leads to the formation of atomic, excited, and ionized species of the process gas as well

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Fig. 1. The schematic drawing of the contact region in ultrasonic wire bonding. (a) The bond ball and the bond pad are approached, leading to asperity contact that plastically deforms under the high contact pressure. The gold ball moves with a velocity, v_0 , over the bond pad. (b) The lateral movement of the piezo horn induces a frictional heating at the interface. Local welding leads to an irregular stick-slip behavior where occasionally formed welding spots form and break. Therefore, the average velocity is $v_1 < v_0$. (c) If the induced heat was sufficient, enough welds have formed to support the lateral force of the piezo horn. A stable bond is formed.

as electrons and radiation.^{5,6} Therefore, by such a process, reactive species can be created without the need for chemical reactions. Furthermore, as the operating pressure of the plasma is usually in the 1 mbar to 10^{-4} mbar regime, the amount of material used for a particular process is very low. Therefore, plasma processes are economically advantageous and ecologically uncritical compared to chemical etching and cleaning procedures that are generally based on hazardous chemicals. Such chemical procedures find their application in the semiconductor industry for chip manufacturing, but plasma processes started to establish themselves in this business for the previously mentioned reasons.

One application for plasmas is the removal of contaminations from bond pads. Different classes of bond-pad materials with respect to contamination can be distinguished.

- Materials that do not form an oxide layer (Au, Pt). On those materials, organic contaminations determine the bonding performance.
- Materials that form a stable oxide layer (Al, Si). The properties of the oxide layer limit the bonding process.
- Materials that form an incoherent or unstable oxide layer (Ag, Cu, and Pd). Materials of this category show bonding characteristics influenced by oxides as well as organic contaminations.⁷

Silver is an important material for electronic contacts because it offers the highest thermal and electrical conductivity in the relevant temperature range for semiconductor chips. Standard pull-force tests showed that silver bond pads undergoing an Ar/H plasma treatment show distinctly improved bondability performance over untreated samples.⁷ This phenomenon was studied using a modified, ultrasonic wire bonder.

A schematic of the setup as well as a characteristic measurement curve is presented in Fig. 2. Instead of using a gold ball for the bonding process, a Ni/Au thermocouple is used in the bondability analyzer. This approach gives direct access to the bond-ball

Fig. 2. (a) The schematic setup of the bondability analyzer head. The Au/Ni thermocouple bond ball is formed by an electrical discharge. (b) The typical measurement of the thermovoltage during a bonding process. The dotted line depicts the excitation of the piezo horn.

temperature during the process. The temperature of the bond ball can be directly related to the frictional behavior of the two interfaces in contact.^{8,9} An alternative design presented by Mayer et al.¹⁰ uses a normal gold ball, and the frictional heating is measured by a specially designed bond-pad chip. This allows the use of an unmodified ultrasonic wire-bonding head but offers significantly lower sensitivity.

The improved bonding properties of the plasma-treated Ag samples were identified to be due to the removal of contaminants from the silver surface. Plasma-treated bond pads offer the possibility to store the surfaces under ambient conditions for days without deteriorating the bondability performance.¹¹ Up to now, this phenomenon was observed but not understood. It was thought that this effect was due to passivation of the Ag surface. It is, therefore, of interest to study the behavior of the silver-oxide system undergoing a H₂ plasma treatment. Studies were made on evaporated Ag as well as Ag single crystals to understand the structural behavior of the silver-oxide system undergoing a H₂ plasma treatment. The measurements on the Ag film were performed on in-situ evaporated Ag on a quartz-crystal microbalance (QCM), giving us insight about the dynamic behavior of the silver/oxide system during the plasma process.

EXPERIMENTAL

Equipment

All experiments were performed in a modified Omicron photoelectron spectrometer equipped with an electron-cyclotron resonance (ECR) plasma source. The base pressure of the system is 5×10^{-11} mbar. Untreated and plasma-treated Ag single-crystal surfaces were investigated by low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS, Mg K_α source), angular-resolved ultraviolet photoelectron spectroscopy (ARUPS, He I source), and x-ray photoelectron diffraction (XPD).

The XPS gives access to the chemical composition and the bonding state at the surface. The XPD and LEED give mainly structural information of the surface. The ARUPS gives access to the valence band of the surface and is very sensitive to surface structure and orientation.

For all plasma treatments discussed here, the gas pressure during the treatment was in the order of 10^{-2} mbar. The average ion energy under this condition is on the order of 1 eV for H ions and 4 eV for O ions as measured by analysis of the ion-energy distribution with an electrostatic ion-energy analyzer.¹² The kinetic energies are below the threshold for sputtering processes. The main function of the plasma is to circumvent the dissociative step of the gas molecules at the surface, providing a high flux of atomic and ionic gas species to the surface.

Sample Preparation

The experiments were performed on Ag(110), Ag(111) single-crystal surfaces, and an Ag film evaporated in situ on a QCM. Experiments up to film thickness of 1 μm showed that the process is not thickness limited as long as the treatment time is adjusted accordingly. The results presented here for the QCM were measured on a 40-nm Ag film. Before undergoing plasma treatments, the single-crystal surface was cleaned by Ar^+ sputtering and annealing cycles. No C or O contaminations could be observed with XPS, and sharp LEED and XPD patterns could be observed, reflecting a clean sample with long-range order. The Ag film was evaporated in situ on a new QCM crystal to eliminate sources of contamination. The silver oxide was formed using an O_2 plasma. By the plasma process, one can form a thick ($> \mu\text{m}$), homogeneous oxide layer in situ under UHV conditions, avoiding any source of organic contamination.¹³ All samples were oxidized in an O_2 plasma for 60 min prior to the reduction step. The samples were reduced by exposure to an H_2 plasma. While the single-crystal surfaces were analyzed by XPS, XPD, ARUPS, and LEED as clean, oxidized, and reduced samples, the Ag film in-situ evaporated on the QCM was studied by the shift in resonance frequency of the quartz crystal during the treatment. The mass uptake is directly related to the resonance frequency through the Sauerbrey equation for rigid films:

$$\Delta f = -\frac{1}{C_f} \Delta m$$

The term C_f is called the Sauerbrey constant and is independent of the film properties. The frequency shift along with the atomic masses served as a basis to calculate the O/Ag ratio of the Ag film.

RESULTS AND DISCUSSION

Oxidation

QCM Measurements

The oxidation of the evaporated-Ag film was monitored during the O_2 plasma treatment and is pre-

sented in Fig. 3. After 60 min of oxidation, the O/Ag ratio was 1.3, thus showing that the oxide formed is Ag_2O with an excess in oxygen. The oxygen content slightly relaxed after switching off the plasma and stabilized at $\text{O/Ag} = 1.2$. XPS, and the ARUPS spectra on the oxidation were presented elsewhere.¹⁴ Evaluation of the O/Ag ratio from the peak integral taking in account the analyzer transmission¹⁵ and cross sections of the respective elements are in agreement with the observations with the QCM and show the formation of Ag_2O .

Photoelectron Spectroscopy Measurements

The XPS spectra were measured on the single-crystal surfaces. The $\text{Ag}3d$ spectra are presented in Fig. 4. The oxidation of the surface leads to a negative peak shift in binding energy of the $\text{Ag}3d$ level. The observed peak shift corresponds to the expected values for silver oxides.¹⁶⁻²¹

H_2 Plasma Treatment

QCM Measurements

The effects of the H_2 plasma on the formerly oxidized-Ag film by QCM are depicted in Fig. 5. The arrow denotes the time when the plasma was switched on. The H_2 plasma treatment results in a complete reduction of the oxidized-Ag film. The convergence of the O/Ag ratio to zero indicates that the observed reduction is a bulk phenomenon. In the first phase of the reduction, a linear decrease in the O/Ag ratio can be observed. Such behavior is to be expected if the reduction is limited by the available flux of H atoms and ions on the surface and not by the diffusion processes. The linear decrease changes into an exponential decay as a function of time at an O/Ag ratio of about 0.5, as indicated by the dashed

Fig. 3. The O/Ag ratio as calculated from the change in resonance frequency of a QCM crystal evaporated in situ with 40-nm Ag and subjected to O_2 plasma treatment. The arrow denotes the time when the plasma was switched off. The O/Ag ratio stabilizes around 1.2, indicating an oxide Ag_2O with excess oxygen. The reduction of the oxygen content after plasma switch-off is most likely due to desorption of surface oxygen.

Fig. 4. The Ag3d spectra as measured by XPS on Ag(111) with Mg K α radiation: (a) clean Ag sample; (b) after oxidation in an O₂ plasma, the peak shift corresponds to the expected binding energy shift for silver oxides; and (c) silver peak after reduction in a H₂ plasma. The peaks are shifted back to their initial position.

Fig. 5. The O/Ag ratio of a formerly oxidized 40-nm Ag film on a QCM crystal during H₂ plasma treatment. The arrow indicates the switching on of the H₂ plasma.

line in Fig. 5. The incoming flux of the reducing species is no longer the limiting factor. The diffusion of O from the bulk in a layer where the reduction takes place limits the reduction rate of the oxide layer.

As the frequency shift does not drop below the initial frequency shift for the clean Ag film, we can safely exclude sputtering as a means for eliminating the oxide layer. Bohdansky et al. have presented a model that describes the sputtering yield as a function of energy.²² In view of the low kinetic energy of the H₂ plasma ions, sputtering is not expected. Already little sputtering of Ag would be easily de-

tectable in the QCM signal because even severe hydrogen uptake would not compensate for little Ag losses because of the high difference in atomic mass between the two elements.

The investigated reaction is, therefore, a bulk reduction of the oxide and not only limited to a surface or near-surface layer.

Photoelectron Spectroscopy Measurements

The XPS spectra in Fig. 4 shows that the Ag3d level shifts back to its initial position during the reduction in a H₂ plasma.

The valence-band spectra as measured by ARUPS presented in Fig. 6 show (a) the Ag(110) spectra along the surface normal; (b)–(d) the Ag(111) spectra along the surface normal, along the [110] direction, and along the [100] direction, respectively; and (e) the Ag(110) valence band after undergoing several oxidation and reduction cycles. From spectra (a) and (b), it is clear that ARUPS depends strongly on the surface termination under investigation. It represents, therefore, a good tool for the study of phenomena depending strongly on crystallographic orientation. The (e) spectra exhibits characteristic features of the (111) surface orientation and can be well fitted using a superposition of spectra (a)–(d). Therefore, we conclude that, after oxidation and reduction cycles on Ag(110), there exist regions at the

Fig. 6. The ARUPS valence-band spectra: (a) clean Ag(110) measured along the surface normal, (b) clean Ag(111) measured along the surface normal, (c) clean Ag(111) in the (110) direction, (d) clean Ag(111) in the (100) direction, and (e) Ag(110) valence band after several oxidation/reduction cycles in O₂ and H₂ plasmas. The valence-band spectra shows features characteristic for the (111) orientation. The spectra (e) can be well fitted by a superposition of the spectra (a)–(d).

surface with a (111) termination in coexistence with (110)-terminated regions.

The (111) surface is the most dense surface orientation, while the (110) plane is the most open of the low index-surface planes. During the reduction, the Ag atoms are highly mobile because of the increase in density from the oxide to the metal. While some regions form a (110) surface because of still present local information about the original crystal structure, other regions start to form a (111) termination because it is energetically favorable to form a densely packed atom layer.

The oxidation of a material in contact with oxygen is determined by the sticking coefficient of the gas molecule and the dissociation rate at the surface. It is well known that the sticking coefficient of O on Ag surfaces is very low, with the (111) termination exhibiting the lowest coefficient ($\sim 10^{-6}$) and the (110) termination exhibiting the highest ($\sim 10^{-3}$) sticking coefficient. Furthermore, oxygen diffusion through the (111) planes is only activated at elevated temperatures ($T > 923^\circ\text{K}$).²³ The passivation effect of hydrogen plasma treatment on Ag can, therefore, be understood as being caused by the formation of regions with (111) termination at the surface. These regions are less prone to reoxidation because of the much-reduced sticking probability of oxygen. Further, adsorbed oxygen can only diffuse through grain boundaries, defects, and the remaining (110)-terminated surface regions. The (111) facets themselves do not allow for oxygen diffusion at room temperature. Also, as the amount of area with (111) termination increases, the amount of (110) termination decreases.

The oxidation increases the layer thickness by a factor of about 2 because of the differences in density between the metal and the oxide.¹³ During reduction, the decrease in volume induces a large mass transport, and the surface has a tendency to reorganize in the lowest energy-surface orientation, which leads to the observed effect. The (110) features could not be observed in similar experiments on the (111) surface, as this orientation is already energetically favorable.

CONCLUSIONS

In this work, we presented the reduction of silver oxide by H_2 plasma treatment. In any case, the oxide film could be reduced, even up to complete bulk-oxidation treatments. Our investigations by dynamic measurements with a QCM prove that the reduction mechanism is a bulk reduction. After the H_2 plasma treatment, the surface is free of any contaminations and bulk Ag oxides are eliminated. The absence of contaminations is favorable in the tribological contact of the bond ball and the sample surface. Reproducible and good bonding conditions are, therefore, created by such a treatment. For Ag(110), a formation of (111)-terminated regions could be observed for multiple oxidation/reduction cycles. The formation of (110) regions on Ag(111) could not be ob-

served. It is known that the (111) plane of silver shows a pronounced lower sticking coefficient to O_2 compared to (110) and limits the bulk diffusion of oxygen to diffusion at defects and grain boundaries. The claimed passivation effect of the Ar/H_2 plasma-cleaning method on Ag can be understood by the tendency of the highly mobile Ag atoms to form (111)-terminated regions during the reduction process. It inhibits the reoxidation of the surface and delays the building up of the critical 3-nm contamination layer above which contact pressure does not suffice to guarantee a metal-metal contact.

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