Exploring Synchrotron Radiation Capabilities: The ALS-Intel CRADA

F. Gozzo[1,2], A. Cossy-Favre[2], B. Triplett[1], H. Fujimoto[1] and H.Padmore[2]
[1] Component Research, Intel Corporation, Santa Clara, California 95052, USA
[2]Advanced Light Source, Lawrence Berkeley National Laboratory,
University of California, California 94720, USA

Synchrotron radiation spectroscopy and spectromicroscopy were applied, at the Advanced Light Source, to the analysis of materials and problems of interest to the commercial semiconductor industry. We discuss some of the results obtained at the ALS using existing capabilities, in particular the small spot ultra-ESCA instrument on beamline 7.0 [1] and the AMS (Applied Material Science) endstation on beamline 9.3.2 [2].

INTRODUCTION

The continuing trend towards smaller feature size and increased performance for semiconductor components has driven the semiconductor industry to invest in the development of sophisticated and complex instrumentation for the characterization of microstructures. Among the crucial milestones established by the semiconductor Industry Association are the needs for high quality, defect free and extremely clean silicon wafers, very thin gate oxides, lithographies near 0.1 micron and advanced material interconnect structures. The requirements of future generations cannot be met with current industrial technologies. The purpose of this ALS-Intel CRADA (Cooperative Research And Development Agreement) is to explore, compare and improve the utility of synchrotron-based techniques for practical analysis of substrates of interest to semiconductor chip manufacturing. The first phase of the CRADA project consisted in exploring existing ALS capabilities and techniques on some problems of interest. We discuss here some of the preliminary results obtained on Intel samples.

EXPERIMENTS AND RESULTS

We performed a high energy resolution XPS study on thin blanket titanium nitride (TiN) films using the scanning ultra-ESCA spectromicroscope on beamline 7.0 [1]. In addition to its original use as an antireflection coating, titanium nitride has been recognized as an important materials component of metallization structures used in advanced microelectronic devices[3]. It improves adhesion and it is an excellent barrier against diffusion. TiN must conform to the extreme topographies used in devices in order to guarantee void-free plug formation and low junction leakage. It also needs to be very thin in order to reduce interconnect stack thickness and minimize contact and via resistance. However, deposition parameters influence the TiN electronic and chemical properties. Thus, it is important to understand the relationship between these deposition parameters and the electronic and chemical properties and ultimately the way TiN behaves as an adhesion layer and a diffusion barrier. It is also important to study the feature size dependence of its properties because step coverage will only become more challenging as feature sizes decrease and the aspect ratios increase.

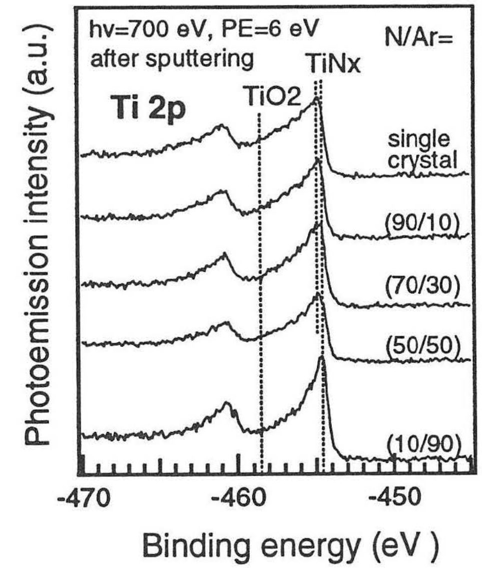

Figure 1. XPS Ti 2p peaks from TiN film with different N/Ar ratios. The signal from a single TiN crystal is taken as a reference.

Figure 1 shows XPS Ti 2p core level peaks from four different TiN films plus a TiN single crystal used as a reference after sputtering the first surface layers. The films were deposited by reactive sputtering at different N/Ar ratio from 10/90 to 90/10. A low N/Ar ratio may give a better conformality associated to a low sputtering rate. However, the sputtering process may be too slow and inefficient and allow a higher impurity level. By contrast, a high N/Ar ratio may result in a high sputtering rate with an excessively low conformality and undesired stoichiometry. The Ti2p structures in Fig.1 are the convolution of at least two Ti2p components. The main component on the lower binding energy side has been identified as Ti2p in a TiN$_x$ bonding. We observe a shift of this component towards higher binding energy for increasing x values, whereas a shift in the opposite direction was observed in the corresponding N1s core levels. The observed shifts are consistent with the expected increase of ionicity in TiN$_x$ as nitrogen atoms are added to the TiN$_x$ compound. The higher binding energy side component should correspond to some Ti oxidation state (TiO$_x$ with $0<x<2$), since we found clear evidence for the presence of oxygen even after sputter cleaning the surface. Oxygen was also found in the TiN single crystal spectra after sputtering.

The need of a good set of XPS data on a clean reference sample for a correct assignment of the XPS peak justified the experiments performed on beamline 9.3.2 using the Applied Materials Science chamber.[2] The main purposes of this experiment were to test a new cleaning procedure which reduces the oxygen and carbon signals and to see how valuable could be a valence band study of TiN films when used to probe the sample stoichiometry and composition. The TiN single crystal surface was first slightly argon etched to remove the natural protective titanium dioxide coating. Then, it was flashed at approximately 700 C for few seconds. Figures 2 and 3 show the oxygen 1s and the titanium 2p XPS core levels. The oxygen peak signal was strongly reduced after the annealing and

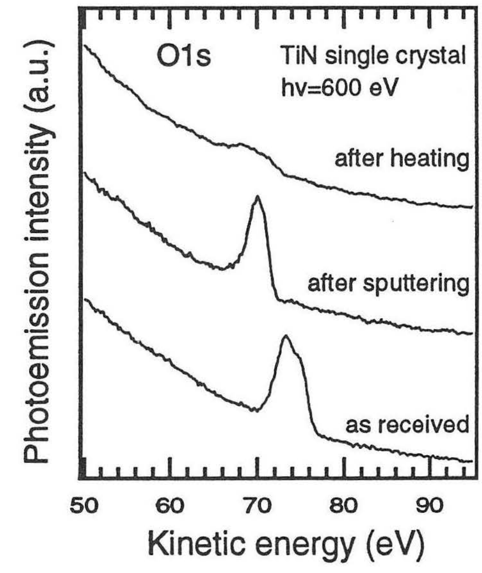

Figure 2. XPS O 1s peaks from a TiN single crystal. Heating the sample at ≈700°C has removed most of the oxygen signal.

the corresponding Ti 2p core levels show a strong change of the peak shape after sputtering and flashing. The second component at the lower kinetic energy side which appears after flashing the sample, may be attributed to a satellite feature as reported by Porte et al.[4] The authors performed a XPS analysis on contaminant-free TiN_x samples for different stoichiometry ($0<x<0.97$). For $x>0.75$, they found a second component at the higher binding energy side of the Ti2p doublet line, which is almost completely absent for lower x values. This component was interpreted as a satellite structure related to the decreasing screening ability of the conduction electrons when the composition approaches the stoichiometric value.

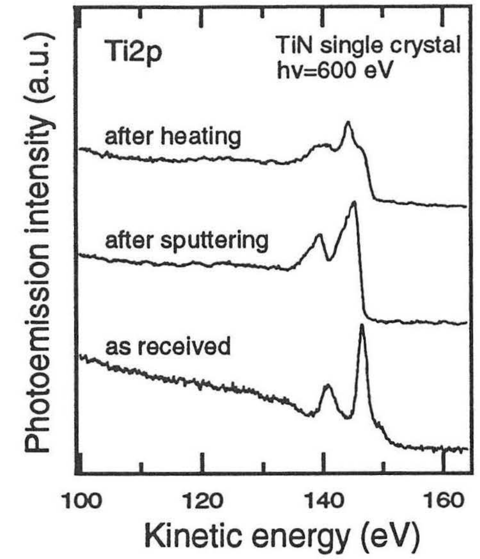

Figure 3. XPS Ti 2p peaks from a TiN single crystal.

Another challenging experiment we performed on beamline 7.0, which took the advantage of the microscopic capabilities of the ultra-ESCA spectromicroscope and of synchrotron radiation, was a depth profiling analysis of a blanket multiple Al/Ti/TiN/SiO_2 interface. We needed to understand the chemistry of the interfaces involved, in particular the Al/Ti interface. Since the sample was a blanket multiple interface, one could simplisticly argue that there was no need for a microscopic XPS. However, an important point which should always be considered when doing depth profiling with a sputter gun, is the extreme difficulties in obtaining uniform sputtered areas over a millimeter scale. When XPS depth profiling is performed with a conventional source, the collected signal is integrated over all the probed areas and does not necessarily correspond to the chemistry under investigation.

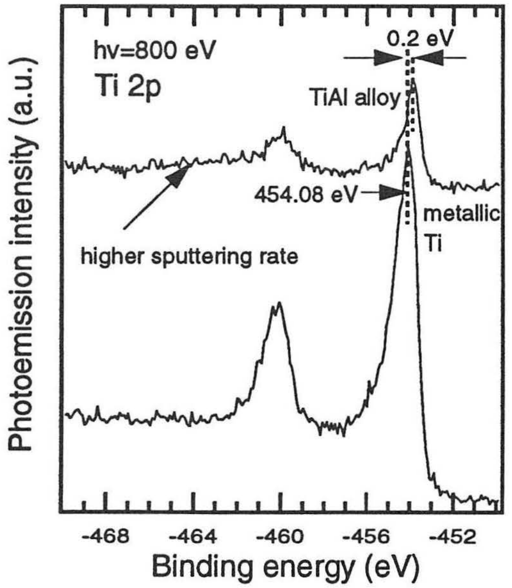

Figure 4. XPS Ti 2p peaks from a Al/Ti/TiN/SiO_2 multiple stack at the Al/Ti interface taken in two different x,y positions. The top spectrum corresponds to a region where the sputtering efficiency was higher.

Our micro-XPS analysis showed evidence of the formation of a Ti_3Al alloy at the Ti/Al interface when looking at the Ti2p core level peak (see Fig.4). Nitrogen was present in both Ti and TiN layers, but where there was the evidence of Ti_3Al alloy formation, no nitrogen was present. Although the corresponding Al 2p core level binding energies were not consistent with the expected values for the Ti_3Al alloy[5], this was expected since the escape depth for Al2p and Ti2p at the given photon energy (800 eV) is quite different and we were probably comparing different sample layers. The different behavior for the Ti2p and the Al2p core levels at 800 eV, in fact, suggests that the chemistry changes rapidly at the interface and it is very complex.

Another topic of great interest for the semiconductor industry is the search for new low dielectric constants materials (low "k" dielectrics). The chip speed is limited by both the resistance of the metal line and the surrounding insulator. Reducing the metal resistance or the insulating capacitance both push towards the same direction: reaching a higher chip speed. Reducing capacitance also helps minimize crosstalk between adjacent metal lines, an increasingly severe problem.[6]

The push to get to lower dielectric constants has led the industry to investigate two basic approaches. The most easily implemented one, which has the attraction of using existing tools, is to introduce fluorine into more or less standard plasma oxide deposition processes, resulting in fluorinated silicon oxides (SiOF). Although there is an important tradeoff between the amount of fluorine added and the stability of the film, dielectric constants of 3.5 and also 3.2 seem to be achievable with acceptable film stability. The other approach is to use carbon based polymers with designer chemistries tailored to achieve the combination of low dielectric constant and high thermal stability. This approach may ultimately allow a more dramatic reduction of the dielectric constant to perhaps 2 or less. For all of these materials it is important to study their potential for performance improvement against thermal, electrical, chemical and mechanical stability issues which pose reliability risks and interfere with their incorporation into the interconnect system. In all cases, the integration of such materials will be a major development in materials science compared with the well understood integration of plasma and CVD (Chemical Vapor Deposition) SiO_2. In the case of the fluorinated silicon oxides, for example, the higher the fluorine content, the lower the dielectric constant. However, the higher the fluorine content, the higher their tendency to absorb water and release fluorine with a consequent monotonic increase of the dielectric constant and the potential to produce delamination, corrotion, and electromigration failures of the metal lines and vias.

We recently performed a comparative depth profiling XPS study on two SiOF films produced by two different vendors and procedures (sample A and B). One SiOF film was capped after deposition in order to

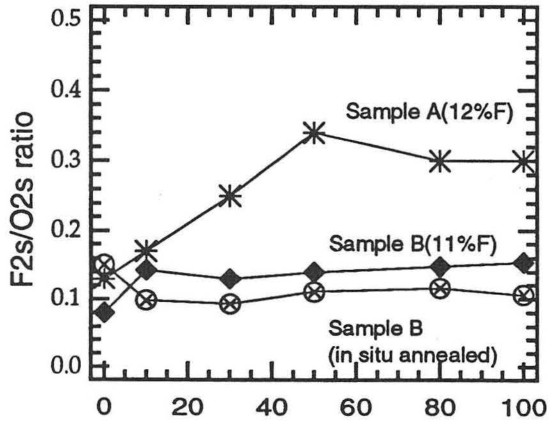

Figure 5. Fluorine over oxygen ratio vs. sputtering time for two SiOF films produced by two different vendors and procedures. Sample b was also *in situ* annealed.

prevent water absorption. Figure 5 shows the fluorine over oxygen ratio as a function of the sputtering time for the two unannealed samples A and B and for sample B after annealing under UHV. Sample A shows the highest F/O ratio and also the strongest variation as a function of the depth profile. The first point value, corresponding to the *as received* sample, is not surprising since sample A was nominally capped. However, the F/O ratio increases rapidly reaching a maximum after 50' sputtering and then it drops and remains quite constant. Different is the behavior of sample B for which the F/O value is quite uniform throughout the film both before and after annealing. Although the sputtering process may have changed the original composition of the film by disrupting some surface chemical bonds, the inhomogeneities observed in the film A should be intrinsic to the film, since the same process does not produce the same effect on the film B.

ACKNOWLEDGMENTS

This work was partially supported by the Swiss National Science Foundation and the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No.DE-AC03-76SF00098. We thank Intel's Materials Technology and Components Research groups for characterizing samples used in the demonstration of the feasibility of X-ray spectromicroscopy applications. We also thank E.Rotenberg, J.Derlinger, S. Cerasari, Xin Zhou and Z.Hussain for their competent help and excellent assistance on beamline 7.0 and 9.3.2.

REFERENCES

[1] J.D.Denlinger, E. Rotenberg, T.Warwick, G.Visser, J.Nordgren, J.-H. Guo, P.Skytt, S.D. Kevan, K.S. McCutcheon, D.Shuh, J.Bucher, N. Edelstein, J.G. Tobin and B.P. Tonner, Rev. Sci. Instrum. **66**(2), 1342 (1995).

[2] Z. Hussain, W. R. A. Huff, S. A. Kellar, E. J. Moler, P. A. Heimann, W. A. McKinney, H. A. Padmore, C. S. Fadley, and D. A. Shirley, J. of Electron Spectrosc. Relat. Phenom. **80**, 401 (1996).

[3] M. Eizenberg, MRS Bulletin **44** (11), 38 (1995).

[4] L. Porte, L.Roux and J. Hanus, Phys. Rev. **B28** (6), 3214 (1983).

[5] D.E. Mercer, Jr, T.R. Hess, T. Mebrahtu, D.L.Cocke and D.G.Naugle, J.Vac.Sci.Technol. A9 (3), 1610 (1991).

[6] P.Singer, Semiconductor International, 88 (May 1996).

Principal investigator: Fabia Gozzo, Component Research, Intel Corporation, SC1-03, 3065 Bowers Ave., Santa Clara, CA 95052. E-mail: FabiaX_Gozzo@ccm.sc.intel.com OR Fabia_Gozzo@macmail.lbl.gov.