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Ion Beam Spectroscopy as a Means of In-situ Monitoring of Thin Film Deposition

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Low energy (5-15 keV) pulsed beam Ion Scattering Spectroscopy (ISS) and Direct Recoil Spectroscopy (DRS) are surface analytical tools which possess the ability to provide a remarkably wide range of information directly relevant to the growth of multi-component semiconductor, metal and metal oxide thin films and layered structures. Ion beam methods have not been widely used for this purpose because the design of existing commercial instrumentation is unsuitable in terms of vacuum requirements, data acquisition rate, geometric interference with the deposition equipment, and the magnitude of the ion beam dose and consequent film damage required for the acquisition of spectra with reasonable signal-noise ratios. Users of advanced custom-built Time-of-Flight (TOF) instruments have been largely interested in other problems and for the most part, unaware of some of the unique operational characteristics of TOF DR/ISS as they pertain to thin film growth. We discuss here some of the physical properties which may be measured by DR/ISS and describe a physical implementation of the technique which is suitable as a real-time probe of thin film deposition in terms of very low required beam dose, rapid data acquisition, physical non-interference with the deposition equipment and high ambient pressure operation.

Introduction

Thin film deposition systems operating on commercial semiconductor assembly lines require some means for *in situ* monitoring of thin film growth, especially as more complicated materials and layered structures are produced for advanced device applications. Two examples of the sort of situation requiring in-situ monitoring are cited here. We have been using a sequential deposition method [1,2] for the production of $YBa_2Cu_3O_{7-x}$ thin films and layered structures. In this method, very thin layers of material are deposited sequentially using elemental, alloy or simple oxide targets. These films may either be partly oxidized during deposition and then subjected to a post-deposition oxygen annealing cycle, or be oxidized more aggressively during deposition to produce a film which is superconducting as-deposited. By deferring the introduction of oxygen in the post-deposition annealing process, films can be routinely produced with transition temperatures (T_c) between 92 and 93 K and very high critical current densities (J_c) [3]. However, these films are subject to extensive pinhole formation. Rapid introduction of oxygen during annealing suppresses pinhole formation, but results in the formation of a small amount of $BaCuO_3$ phase, and T_c and J_c are somewhat lowered. The trade-off between impurity phase formation and pinhole formation appears to be a very complicated one in which detailed knowledge of the mechanisms would be very beneficial. The as-deposited films are free from pinholes, but generally have lower T_c and J_c values than the post-annealed films. It appears that these films are subject to ion beam damage during deposition [4]. Consequently, it is important to know the defect density of the film as it is being deposited.

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Techniques such as x-ray diffraction and x-ray fluorescence spectroscopy can be used for *in situ* characterization of the overall properties of a film, but they sample the material to a depth exceeding the thicknesses of most thin films, and are not useful for multilayer structures. In order to characterize the process occurring at the surface of a growing film, it is necessary to probe the first few atomic layers, and in principle to identify the uppermost monolayer where the growth occurs. All surface analysis schemes involve directing ions, electrons, or photons onto the sample, and detecting the ejected ions, electrons, or photons resulting from a number of different physical processes within the solid. For example, X-ray Photoelectron Spectroscopy (XPS) involves the impact of an incident x-ray beam on the analyzed material to create photoelectrons. The surface sensitivity of XPS is due to the fact that only photoelectrons generated in a very shallow layer near the surface can escape to the vacuum to be detected. However, if there is an ambient gas pressure associated with the deposition process, the short electron mean free path becomes a disadvantage since the electron must travel distances on the order of 0.5 meters through an energy analyzer before it reaches the detector. Techniques such as Auger Electron Spectroscopy (AES), Ultraviolet Photoelectron Spectroscopy (UPS), Low Energy Electron Diffraction (LEED), and XPS typically require ultra-high vacuum ($<10^{-8}$ torr) in the region surrounding the sample.

There is an additional practical constraint on most surface analytical methods as applied to in-situ monitoring of thin film deposition: i.e., the analysis equipment must not intrude in the area occupied by the deposition equipment, and the deposition equipment must have unobstructed line-of-sight to the substrate. In order to obtain relatively high data acquisition rates, most surface analytical equipment requires the positioning of large instrumentation very close to the sample surface. There are several techniques which utilize relatively collimated beams and therefore do not interfere with the deposition process. Reflection High Energy Electron Diffraction (RHEED) utilizes elastically scattered electrons with a kinetic energy in the range of 20 keV. This energy is high enough to provide a reasonably long electron mean free path. RHEED is therefore widely used in molecular beam epitaxy (MBE) systems where the ambient pressure during deposition is relatively low. RHEED provides a measure of the lattice spacing in the direction normal to the substrate, but provides no chemical identification and no information on short-range phenomena such as pinhole formation.

The range of information obtainable by Direct Recoil (DRS) and Ion Scattering Spectroscopy (ISS) probably exceeds that obtainable by any other surface analytical technique. Ion Scattering Spectrometry was demonstrated to be a useful means of thin film analysis by McKinney and Frankenthal in 1973 [5]. This study used ISS as a means of characterizing 20-30 Å thick passivation layers on Fe-Cr alloys. However, it has not been widely used for this purpose for a number of reasons: Early ISS instruments required a very high beam dose, sometimes exceeding the number of atoms at the surface of the film being analyzed in order to produce usable spectra. Data acquisition times could be longer than the film deposition time. Additionally, most ISS analyzers including even currently marketed commercial instruments are geometrically incompatible with almost every conceivable deposition process. Because of the extreme surface sensitivity of the technique, it is commonly perceived as suitable only for use in ultra-high vacuum and therefore incompatible with many thin film deposition methods. Modern Time-of-Flight ISS instruments are either not in fact subject to most of these limitations, or can be modified to correct these difficulties. However, ToF instruments are still relatively rare, existing only as custom-built units in a few laboratories.

The method of ion beam surface analysis consists of directing an ion beam of mass M_1 , kinetic energy E_0 at the surface, consisting of atoms with mass M_2 , and detecting either the backscattered primary particles at energy E_1 (ISS), or the direct recoil-sputtered

surface atoms (DRS) with energy E_2 . For primary ions in the approximate range 1-100 keV, the primary ion-target atom collisions are adequately described by two-body elastic collision dynamics. The kinetic E_1 energy of the scattered primary is then given by

$$\frac{E_1}{E_0} = (1+\alpha)^{-2} [\cos \theta_1 \pm (\alpha^2 - \sin^2 \theta_1)^{1/2}]^2 \quad (1)$$

provided $M_2 > M_1$. The kinetic energy E_2 of the recoil-sputtered surface atom is

$$\frac{E_2}{E_0} = 4\alpha (1+\alpha)^{-2} \cos^2 \theta_2 \quad (2)$$

where $\alpha = M_2/M_1$ and θ_1 and θ_2 are the scattering and recoil angles respectively.

For thin film applications, it is necessary to obtain the data over periods of time which are short compared with the time required for the thin film deposition process, using ion beam doses which result in negligible sputtering or other modification of the surface being studied. Since there are roughly 10^{15} atoms/cm² at the surface of a typical solid, a non-damaging dose may be taken as approximately 10^{13} ions/cm². The kinetic energies of the scattered primary and direct recoil atoms are typically measured either by using an electrostatic energy analyzer (ESA) [5] with a continuous beam, or by pulsing the beam and measuring the time required for the scattered/sputtered particles to reach the detector after the ion beam strikes the sample [6]. The ESA detects only ions, which typically constitute between 0.1 and 10% of the total flux leaving the sample. Moreover, at any given time, the ESA is set to transmit only a very narrow range of kinetic energies, and the spectrum is obtained by scanning this energy window. The ToF scheme, which independently detects both ions and neutrals corresponding to all M_2 values simultaneously, gains 3-4 orders of magnitude in terms of the reduction in data acquisition time and ion beam dose necessary to obtain data. Low beam dose and rapid data acquisition are key requirements for real-time, low damage *in situ* analysis of thin film growth.

The ToF-ISS method consists of directing a pulsed beam of energetic ions onto the surface and detecting the scattered primary particles, most of which are scattered as neutral atoms. If the scattered neutrals are detected, the method has a depth sensitivity of 3-5 atomic layers. However, since the neutralization probability for an ion penetrating more than one monolayer into the solid is nearly unity, the detection of the ion species provides a sensitivity only to the uppermost atomic layer of the solid [7]. This capability is unique among surface analytical techniques. Furthermore, by varying the angle of incidence of the primary beam so that atoms in the second and third layers are "shadowed" by atoms in the first layer, it is possible to determine the distance and bond angle between atoms in the first few atomic layers [8]. Therefore, ToF-ISS is not only capable of measuring the average lattice spacing, but unlike the more conventionally used RHEED, it is element specific, and can thus map out the detailed crystal structure of the first several atomic layers.

The shape of the scattering peak for any given element, and the variation of that shape with primary beam energy and angle of incidence is related to both the lattice defect density [9], and the concentration variation of that species with depth over the first several atomic layers [10]. Varying the angle of ion beam incidence from grazing to normal shows pronounced intensity oscillations in the signal corresponding to subsurface atoms, resulting in peaks which may be identified with specific lattice sites [11,12]. However, atomic species which reside solely on the surface display no intensity variation with angle of incidence. It is therefore possible to distinguish between atomic species which truly reside

on the surface from species for which the concentration varies with depth. By varying both the azimuthal and polar angle of incidence, it is possible to generate atomic images similar in information content to those produced by the Scanning Tunneling Microscope [12].

By placing a detector in the forward scattering direction, surface atoms ejected by direct recoil sputtering are seen in addition to the scattered primary beam. Detection of these recoil-sputtered atoms constitutes the basis of the closely related Direct Recoil Spectroscopy (DRS) analysis technique. ISS provides no signal for ions lighter than the probe beam, but DRS is one of the few surface analytical techniques which is sensitive to helium and hydrogen, and is able to distinguish between H and D at levels down to about 1% [13].

Because of the long source-detector distances associated with the ToF detection scheme, the analysis method does not interfere with the equipment required for the thin film deposition process. The scattering mean free path of low keV ions is much longer than that of sub-keV electrons and ToF-DR/ISS is therefore much more tolerant of high background pressures than most other surface analytical methods. It is also possible to provide differential pumping of the incoming and outgoing ion beam paths to extend the pressure limits of the ToF ion beam techniques even further. This capability has been demonstrated for diamond-like films during growth by Low Pressure Chemical Vapor Deposition (LPCVD) at pressures up to 1 Torr, and hydrogen adsorption has been measured on (100) diamond at ambient pressures up to 330 mTorr with very little loss of resolution [13]. This represents a 6-8 order of magnitude increase in the permissible operating pressure compared with other surface analytical methods.

We describe here a differentially pumped pulsed ion beam surface analysis system, which is designed for use as a combined Direct Recoil and Ion Scattering *in situ* probe to monitor the growth of multicomponent metal, metal oxide or nitride films.

Experiment

The Time-of-Flight Direct Recoil and Ion Scattering Spectrometer (ToF-DR/ISS) system currently under development at Argonne has been used to demonstrate extremely low dose surface analysis, high data acquisition rate, and considerably greater flexibility of operation than previous designs. A thin film growth chamber based on the Single Beam Multiple Target (SBMT) sequential ion beam deposition technology [1,2] has been added as an appendage to the ion beam analysis chamber, permitting real-time monitoring of the growth of multicomponent metal and metal oxide thin films and layered structures. Results obtained with this deposition system will be presented elsewhere [14]. However, in this preliminary study, stainless steel will be used as a reference sample.

The ion beam line is shown in Fig. 1 and consists of an Atomika telefocus ion source injecting a 5-12 keV mass-analyzed ion beam into a transfer tube containing two deflection regions separated by a drift space. Four apertures may be adjusted *in situ*, selected from 6 sizes ranging from 250 μm to 4 mm in diameter. With the 4 mm aperture, a dc beam current of 1-2 μA may be directed a distance of approximately 1 meter through the beam line onto the sample at 10 keV without any intermediate focusing optics. A final optics stage consisting of an ion lens and deflection plate assembly is added for demagnifying the image of the final aperture and rastering the beam to produce a uniform current density over the analyzed area. The voltage pulses applied to the two sets of deflection plates are of fixed width, with a rapid rise time (~ 10 nsec). The time between the leading edge of the first pulse and the falling edge of the second pulse determines the temporal width of the ion beam pulse, which can be altered under computer control over a range of ~ 10 -1000 nsec in

order to to optimize the data collection needs of the experiment. This flexibility provides great control over the type of information which can be obtained from the data.

The analysis system has five detectors, of which four are differentially pumped small area detectors consisting of channeltron multipliers with an entrance cone 1 cm in diameter. These detectors are positioned 50 cm from the sample, and have a geometric collection efficiency of 5×10^{-5} . Two of the small area detectors are in the backscattering direction, one off-axis and the other in line of sight with the sample, permitting simultaneous detection of both ion and neutral backscattering signals. It is useful to refer to the latter signal as the "Neutral Scattering Spectroscopy" (NSS) signal. The other two detectors are in the forward direction, where they function as Direct Recoil (DR) detectors. Differential pumping is capable of permitting DR analysis of samples which are at ambient pressures approaching one Torr, as shown by Fig. 2 [13].

The fifth detector is a 40 mm channel plate with a segmented anode collector consisting of 8 concentric rings, each connected to a separate preamplifier and discriminator. Each segment corresponds to scattering into a well-defined polar angle, and therefore a peak in the ToF spectrum of a given segment corresponds to a well-defined surface species with mass M_2 . The mass resolution is the same as the differentially-pumped small area detectors but the count rate is 64x higher (or equivalently, the required beam dose is 64x lower), resulting in a geometric detection efficiency of 3.2×10^{-3} . Results presented here were all taken with the small area backscattering detector.

The transmitted ion pulse forms a footprint on the sample surface consisting of a stationary "hotspot" along with a much less intense broader spot which moves as the beam is pulsed. For long ion beam pulses and short rise time deflection voltage pulses, the broad spot arising from the tail of the chopped ion beam becomes negligible. The beam spot is therefore spatially stable and well collimated. The beam can therefore be focused and rastered across the surface, functioning as an ISS microprobe. Because of the high count rate associated with the use of long pulses and the large area detector, reasonably short data acquisition times of scanned images are possible, limited primarily by the speed with which the computer is able to read the data from the histogram memory and assemble the images. A detailed description of the ion optics of this system is presented elsewhere [18]. The results presented here were all taken with the unfocused beam using the 1 mm aperture, resulting in a spot ~ 1 mm in diameter at the sample.

One of the most obvious uses of an in-situ thin film surface analysis technique is to monitor the composition of the growing film. By simultaneously collecting signal corresponding to both the scattered neutrals and scattered ions, compositional information may be obtained for both the immediate surface and subsurface species. In either case however, the data is more surface specific than that produced by other "surface" analysis techniques such as Auger electron spectroscopy. This situation is evident in the 10 keV Ne^+ NSS spectrum (Fig. 3) of sulfur which has segregated to the surface of a stainless steel 304 sample. Although S is the dominant species in this spectrum, an Auger spectrum taken on the same sample shows a 6:1 Fe:S ratio. The ISS data is more surface-specific than the Auger data, which samples the iron over an e-folding length of approximately 10 Å.

A key feature of the DR/ISS system developed at Argonne is the ability to arbitrarily alter the length of the ion beam pulse under computer control without modifying the beam

line hardware. It is therefore possible to adjust the pulse length to suit the needs of the measurement. A short ion beam pulse (50-100 nsec) provides high mass resolution and exhibits a distinctly asymmetric peak as shown in Figs. 3, 4a and 5. This asymmetry has been observed in DRS [10], and is ascribed to multiple scattering from subsurface atoms, but has not been reported in the ISS literature. However, most existing ToF ISS/NSS instruments have a fixed resolution which is determined by the beam aperture size and the rise time of the deflection pulse, and can not be easily varied. The beam line geometry is typically fixed at some compromise between resolution and count rate. However, the peak shape contains useful information on the depth distribution of each element. If the interface between film and substrate is not sharp, i.e. if the dominant surface species extends into the substrate, the signal corresponding to the backscattered neutral will have an asymmetric lineshape with a long time-of-flight "tail" resulting from scattering from atoms 2-3 layers below the surface. Since the backscattered ion (ISS) signal is strictly representative of the composition of the uppermost atomic layer, the formation of a coherent film is therefore indicated by the disappearance of scattered ion signal from the substrate. By comparing the ISS and NSS peak intensities and line shapes, it is therefore possible to detect the formation of islands and pinholes in layers only a few Å thick. Such depth-specific information is of paramount importance in the deposition of many HTSCs in conjunction with other materials for device fabrication since the superconducting coherence length may be less than 5 Å, and HTSC devices will therefore require abrupt interfaces between smooth and pinhole-free films only a few Å thick.

A long ion beam pulse results in reduced mass resolution, but provides significantly increased count rate. In many cases the mass resolution is still more than adequate to provide elemental analysis as shown in Fig. 4b. In the case of stainless steel, a 500 nsec Ar⁺ ion pulse is able to completely resolve Fe and Cr, with a total data acquisition time of 93 seconds. No special care was taken to minimize the beam dose for the spectra shown in Figs. 4a and 4b which were both taken using a dose of approximately 3×10^{12} ions. In fact, the signal/noise is much greater than needed for most purposes. Fig. 5 shows a spectrum with a s/n ratio of approximately 20:1, taken with a 50 nsec pulse at a dose of $< 1 \times 10^{10}$ ions. Installation of the large area detector and moderate beam rastering is expected to reduce the required dose and data collection time an additional 2-3 orders of magnitude.

Conclusion

Pulsed ion beam surface analysis provides a number of different types of information relevant to key properties of thin films and ultra-thin layered structures. The operational aspects which have kept the technique from being used to characterize thin film growth, beam damage, long data acquisition times, physical interference with the deposition equipment, and inability to operate at pressures required by the deposition process for many materials, can be overcome by appropriate instrument design.

Acknowledgements

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Figure Captions

Fig. 1 Schematic of the Double Pulse Edge Transmission (DPET) ion beam line. Pulse A is applied to the first deflection region and pulse B is applied to the final deflection region. The interval between voltage pulse A and B determines the length of the ion beam pulse.

Fig. 2 Direct recoil spectrum of hydrogen on diamond (100) as a function of temperature (a) in vacuum and (b) at an ambient pressure of 330 mTorr. The large line is the primary ion beam, and the entire spectrum is produced twice per scan as a result of an unblanked flyback. (From ref. 9)

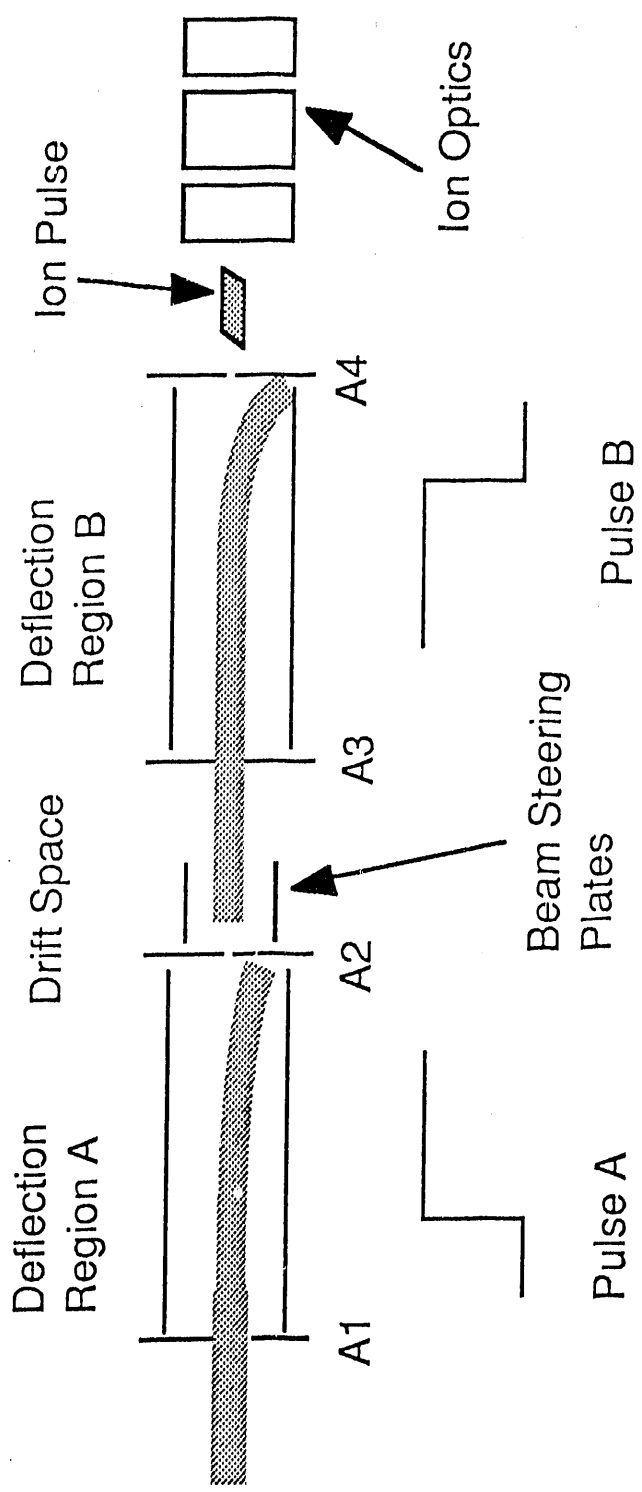
Fig. 3 10 keV Ne⁺ ISS spectrum of a stainless steel 304 sample. Ion beam pulse length = 100 nsec.

Fig. 4 10 keV Ar⁺ ISS spectrum of a stainless steel 304 sample. (a) Ion beam pulse length = 100 nsec. (b) Ion beam pulse length = 500 nsec. Data acquisition time = 93 sec. Total dose for both spectra was $\sim 3 \times 10^{12}$ ions.

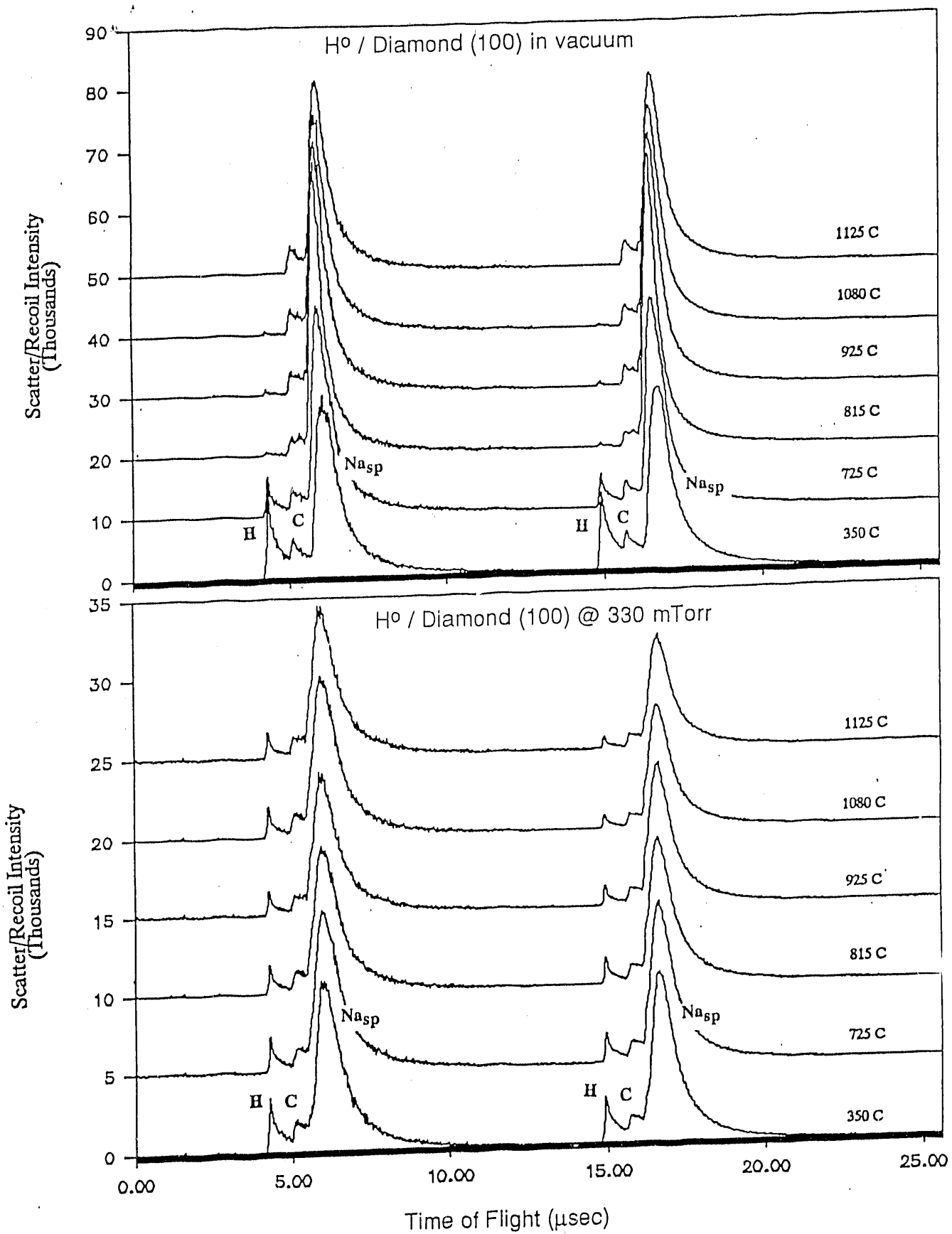
Fig. 5 10 keV Ar⁺ ISS spectrum of a stainless steel 304 sample. Ion beam pulse length = 50 nsec. Average beam current = 12 pA. Total dose was $\sim 1 \times 10^{10}$ ions.

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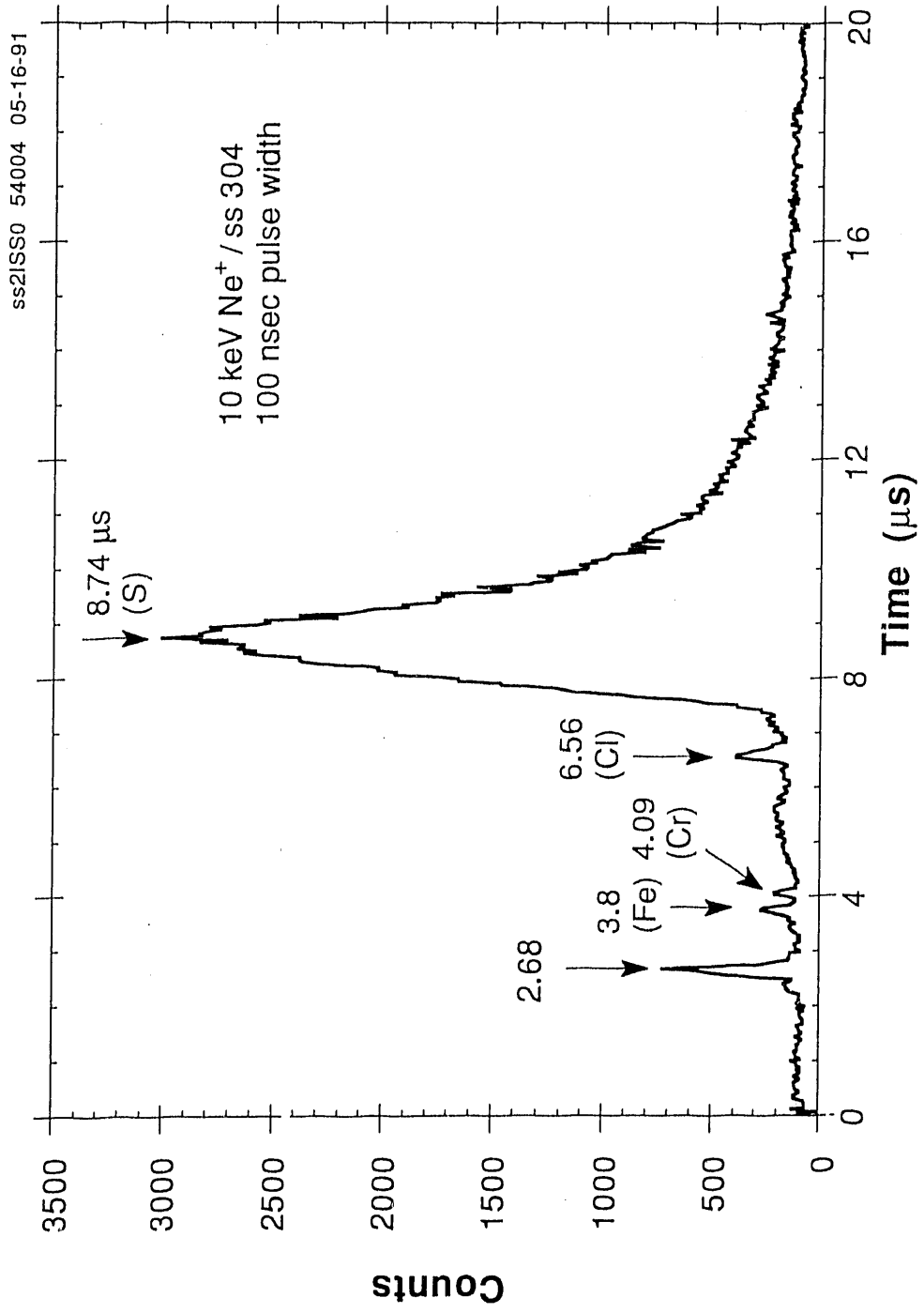
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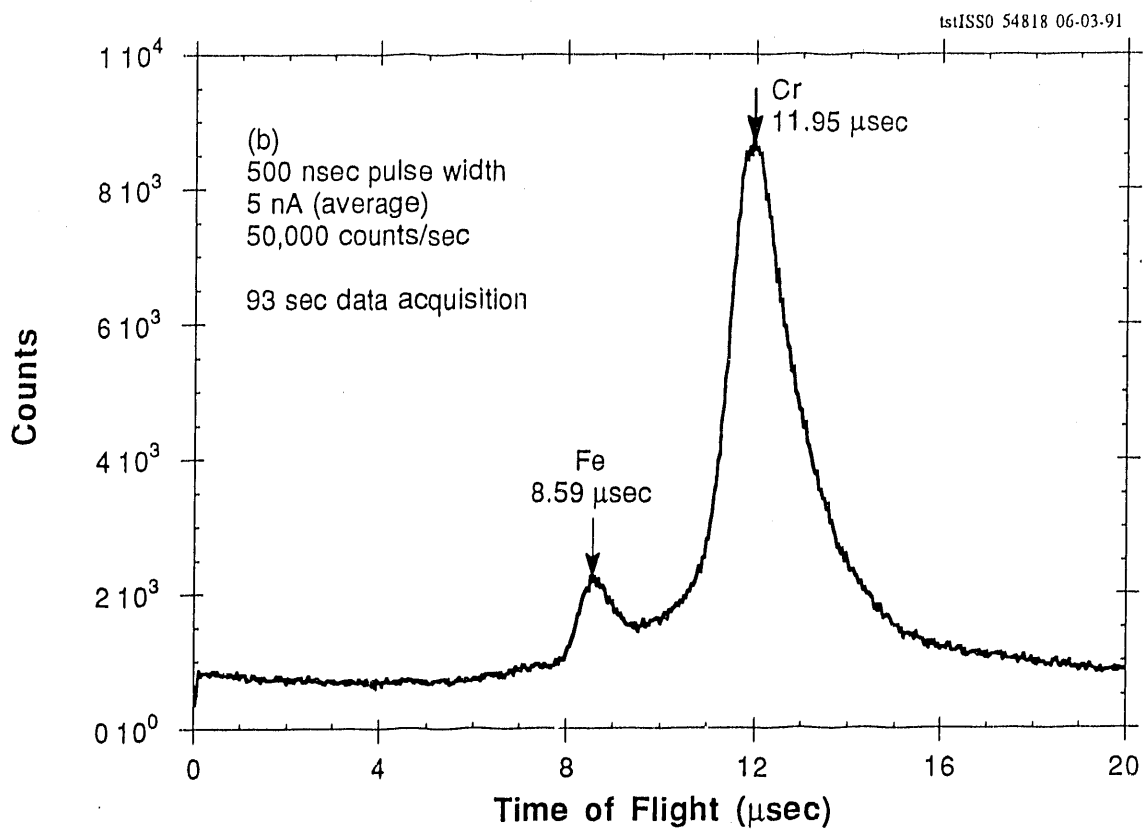
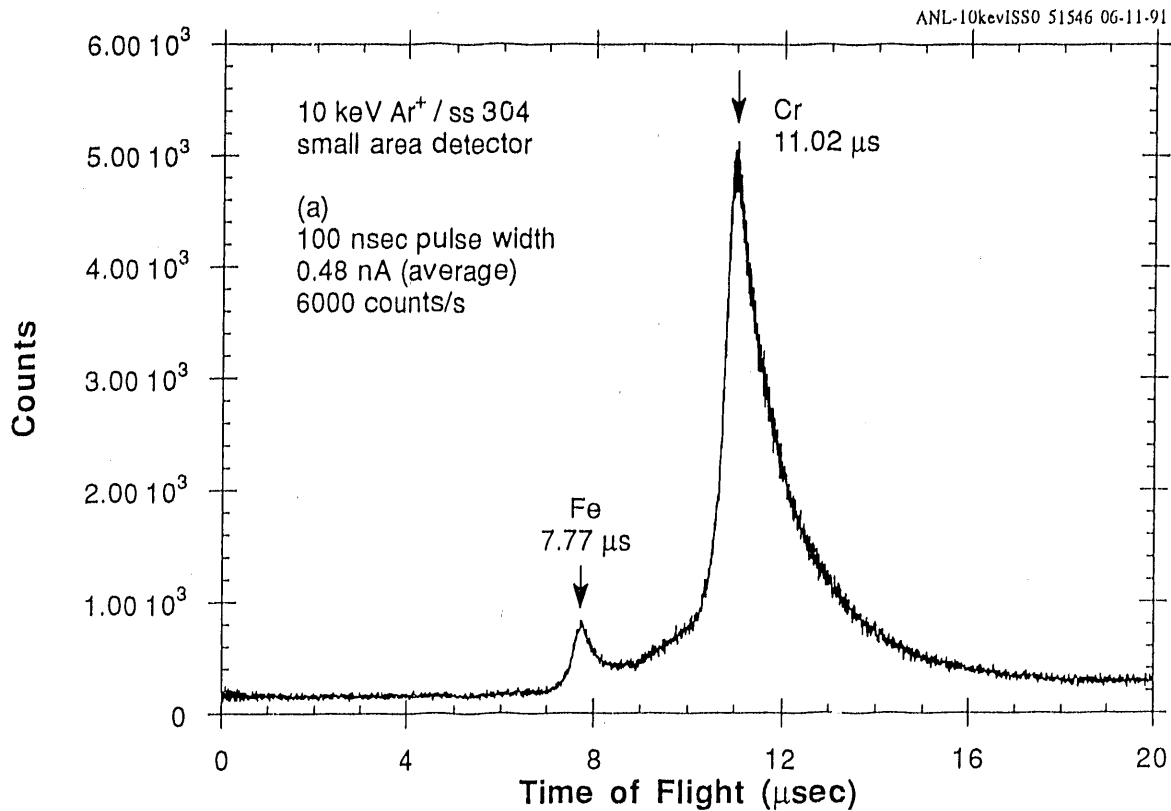


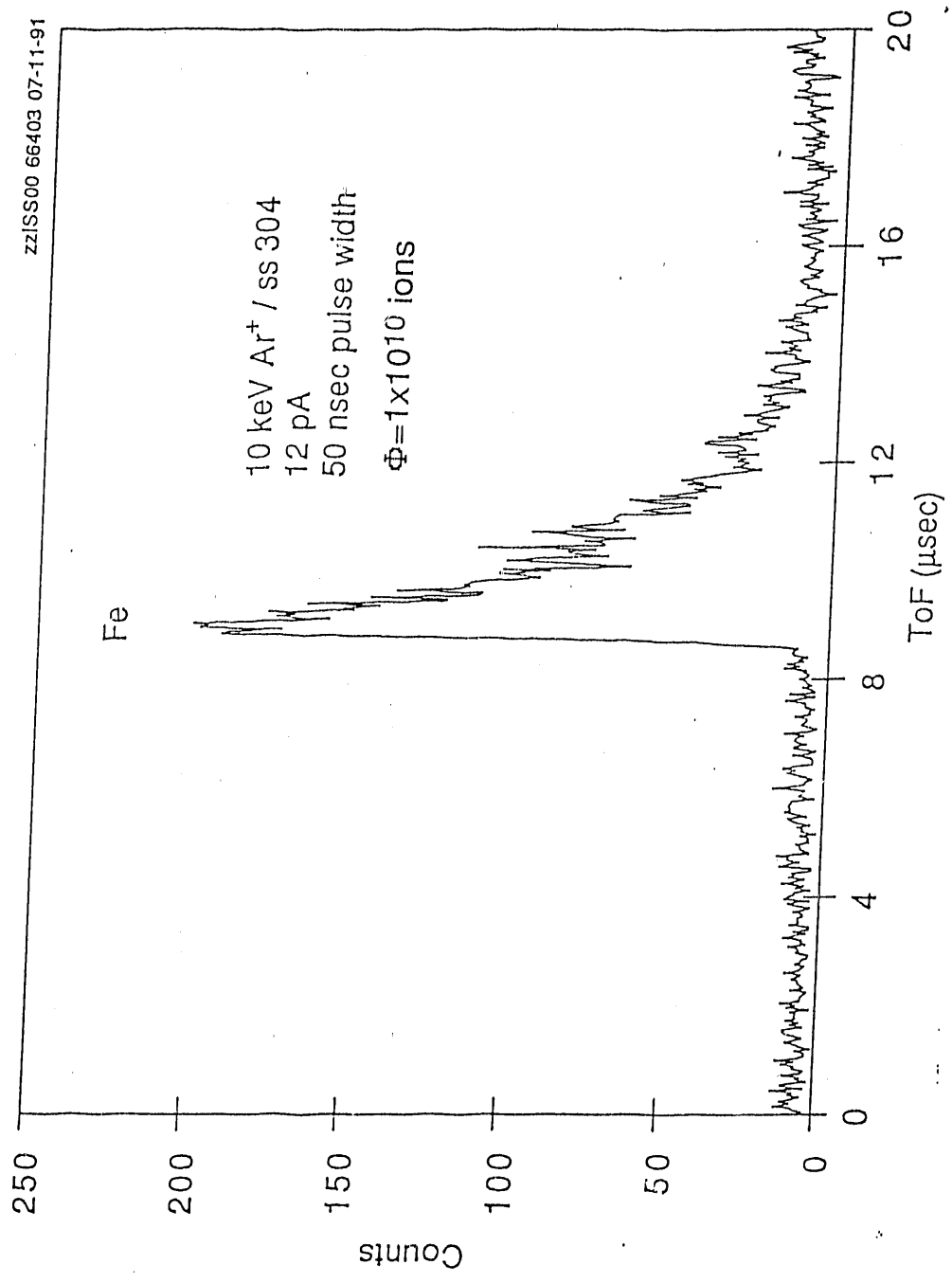
Krauss et. al. Fig. 1



Krauss et. al. Fig. 2







Krauss et. al., Fig. 5

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