APPLICATION NOTE

Investigating the Mechanism of Defect Formation on Aging Paper

The long term stability of paper-based documents, such as manuscripts and artwork, is influenced by the chemistry of the paper itself and also by the conditions of the environment in which the paper is stored. Foxing (small reddish-brown spots observed in many old documents, books, stamps etc) or mold growth, for example, is encouraged by storing paper in a high humidity environment.[1] The mechanism of defect formation on a paper sample stored in a warm, high humidity environment for over 40 years was investigated using the Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectrometer (XPS) System.

Thermo Scientific K-Alpha

Defining the Analysis

An optical image of the paper defect is shown in Figure 1. The image was acquired using the Live Reflex Optics system, found only on K-Alpha. With this system, the user can confidently select analysis points for large or small area XPS analysis. The XPS probe is accurately replicated on the live optical view, allowing the user to easily select the most appropriate probe size for the feature of interest.

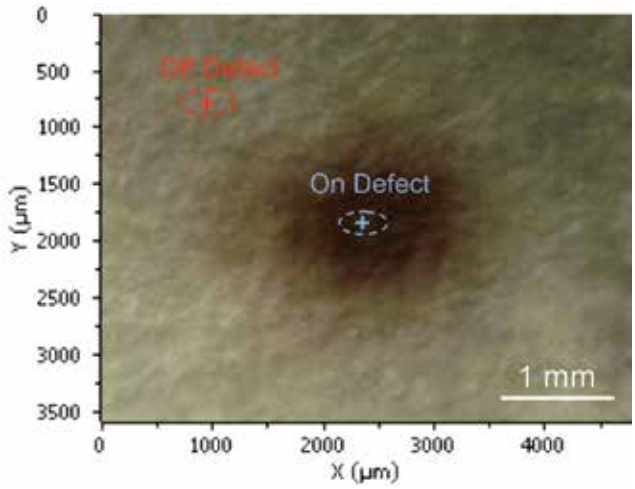

Figure 1: Live optical image of defect in the analysis position of K-Alpha. The ellipses indicate the position and size of the analyzed area.

Elemental Composition of Defect

XPS survey spectra (Figure 2) were acquired from the On Defect and Off Defect areas marked on the optical image. These survey spectra allow the elemental compositions of the paper at the two analysis areas to be quantified (see Table 1).

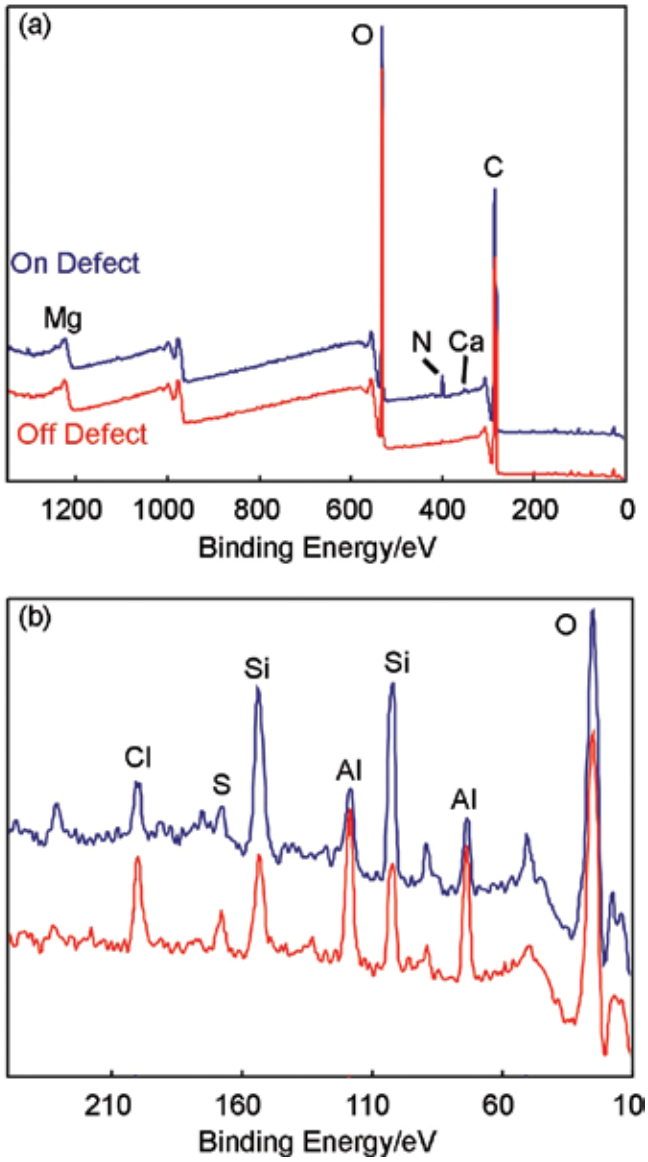

Figure 2: (a) XPS spectra acquired from defect (blue) and off defect (red). (b) Low binding energy region. Spectra have been normalized and offset for clarity.

	Atomic Concentration	
Element	On Defect	Off Defect
Al	0.79	1.32
C	64.91	65.67
Ca	0.28	0.15
Cl	0.17	0.30
Mg	0.32	0.12
N	2.76	0.43
O	29.37	31.15
S	0.09	0.12
Si	1.32	0.75

Table 1: Atomic composition of paper and defect

Both on and off the defect, the elemental composition is dominated by C and O from cellulose in the paper and adventitious carbon contamination on the surface. Several minor elemental components are also observed. The likely source of Al, Mg and Si are coatings such as alumina and talcum. The defect is depleted in Al but has more Mg and Si than off the defect.

Chemistry of Defect

The increased nitrogen concentration at the defect is of particular importance when considering the mechanism of its formation. If the defect was caused by some fungal growth, for example, increased levels of nitrogen-containing amine or amide functionalities would be expected at the defect site.

The nitrogen chemistry of the defect was investigated using high energy resolution XPS spectroscopy. Deconvolution of the nitrogen spectrum (Figure 3) indicated that there were at least two chemical states of nitrogen at the defect. The binding energy of the principal component is consistent with amine or amide functionality. The weaker component is shifted to higher energy and may be assigned to nitrogen in a more oxidized chemical environment.

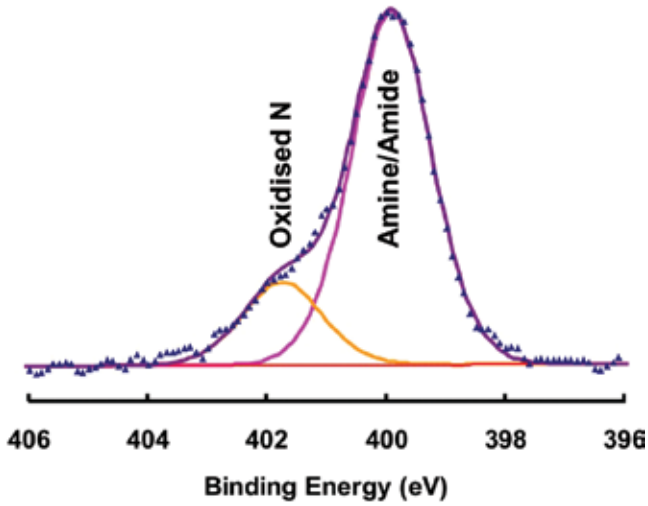

Figure 3: High energy resolution spectrum of nitrogen acquired from defect

Mapping the Defect

The distribution of nitrogen across the paper sample was inves-tigated by XPS mapping. The map (Figure 4) confirms that there is nitrogen across the whole of the paper surface but the defect has a significantly higher nitrogen concentration.

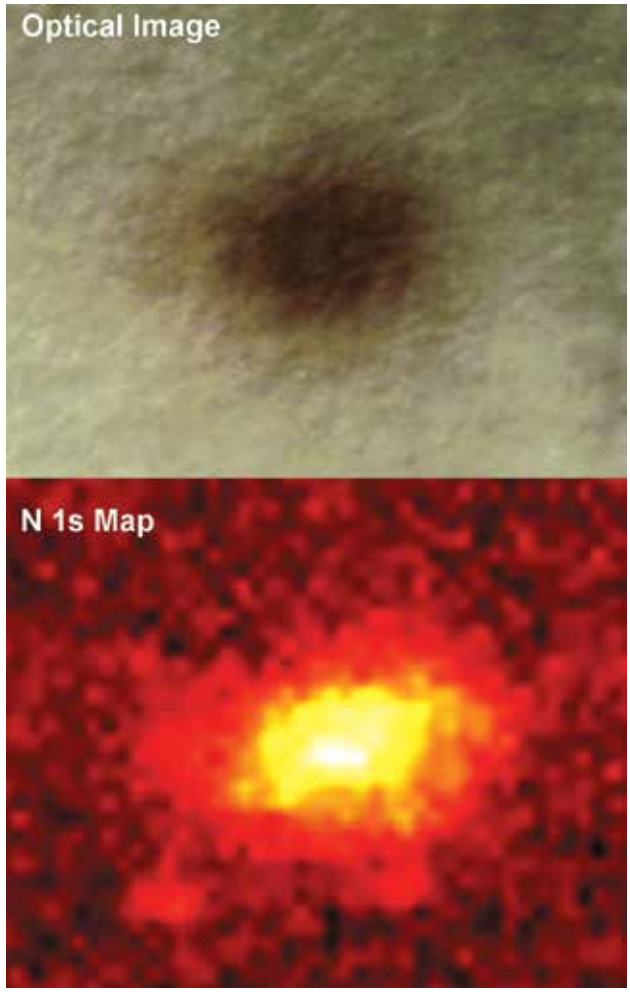

Figure 4: Optical image and nitrogen map across defect

Conclusion

K-Alpha was used to investigate the mechanism of defect formation on paper stored under warm, high humidity conditions for 46 years. The analysis showed that the defect was due to fungal growth, as indicated by an increased nitrogen concentration at the defect site.

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Notes

Keywords
K-Alpha, Adhesion, Contamination, Imaging, Mapping, Surface Analysis, XPS

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